REPORT DOCUMENTATION PAGE

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4. TITLE AND SUBTITLE **The First International Workshop on Flame Chemistry**	**5a. CONTRACT NUMBER** **FA8655-12-1-2065**
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12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution A: Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

In order to find solutions for energy security, alternative fuels, and advanced propulsion systems and to increase energy conversion efficiency and reduce emissions, understanding of new combustion regimes involving new fuels at extreme conditions such as high pressure, low temperature, near flammability limit, high Reynolds number, and high speed in gas turbines and after burners is needed. It is of great interest to develop predictive tools and models to address combustion chemistry and its interaction with turbulent flows at extreme conditions to achieve accurate control of ignition timing, heat release rate, flame instability as well as emissions.

This workshop will assemble worldwide experts in flame chemistry who will:
(a) review the recent progress in the field,
(b) identify the pathways for the development of predictive high¬ pressure flame chemistry in turbulent flows, and
(c) establish a collaborative research relationship.

15. SUBJECT TERMS

EOARD, Flame Chemistry

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1st Workshop on
Flame Chemistry

The First International Workshop
on Flame Chemistry

July 28 - 29, 2012,
Warsaw, Poland

PROGRAM

July 28 (Sat), 2012

7:45 – 8:30 AM Breakfast
8:30 – 8:35 Welcome: Hai Wang and Yiguang Ju

Session 1: Flame Chemistry and Transport

Chair: **Chung K. Law** *(Princeton University, USA)*

8:35 – 9:10 AM Laminar Flames and the Role of Chemistry and Transport
Yiguang Ju and **Sanghee Won** *(Princeton University, USA);*
Zheng Chen *(Peking University, China)*

9:10 – 9:45 Turbulent Flames and the Role of Chemistry
Matthias Ihme (University of Michigan)

9:45 – 10:10 Micro reactor with prescribed temperature profile
Kaoru Maruta (Tohoku University)

10:10 – 10:30 Coffee Break

Session 2: Elementary Reactions and Kinetic Mechanisms at High Pressure

Chair: Charlie Westbrook (Lawrence Livermore Lab, USA)

10:30 – 11:05 Predictive Theoretical Elementary Reaction Kinetics and its Role in Combustion Modeling

Stephen J. Klippenstein *(Argonne National Lab, USA)*

11:05 – 11:40 Kinetic Mechanism Development for Hydrocarbons and Oxygenated Fuels

Henry Curran *(National University of Ireland, Ireland)*
Philippe Dagaut *(CNRS Orleans, France)*

11:40 – 12:15 High Pressure Kinetic Mechanisms for Hydrogen and Hydrogen Syngas

Michael P. Burke *(Argonne National Lab, USA)*
Frederick L. Dryer *(Princeton University, USA)*

12:15 – 13:30 Lunch

Session 3: Uncertainty Quantification

Chair: **Bill Green** (Massachusetts Institute of Technology, *USA)*

13:30 – 14:05 Determination of the joint uncertainty domain of rate parameters:

The case study of hydrogen combustion

Tamas Turanyi *(Eötvös University, Hungary)*

14:05 – 14:40 The role of uncertainty quantification within kinetic model improvement in combustion

Alison S. Tomlin *(University of Leeds, UK)*

14:40 – 15:15 Mechanism Optimization

Hai Wang (University of Southern California, USA)

15:15 – 15:35 Coffee Break

15:35 – 17:30 **Group Discussion Session**: Identification of roadmap, challenges, & collaborations
Elementary Kinetics: Chair, **Robert S. Tranter**

(Argonne National Lab, USA)

Mechanism: Chair, **Matt Oehlschlaeger**

(Rensselaer Polytechnic Institute, USA)

Flame Chemistry: Chairs, **Zheng Chen**

(Peking University, China)

Timothy Ombrello

(Air Force Research Laboratory)

17:30 – 18:30 **Poster Session**

18:30 – Reception

July 29 (Sun), 2012

Session 4: Combustion Diagnostics

Chair: **Nils Hansen** *(Sandia National Lab, USA)*

8:30 – 9:05 Measurements of Elementary Rate Constants, Ignition Delay and Species Histories in Shock Tubes

Ronald K. Hanson *(Stanford University, USA)*

9:05 – 9:40 The role of advanced diagnostics in combustion chemistry research

Katharina Kohse-Höinghaus* *(University of Bielefeld,Germany);*
Fei Qi *(University of Chinese Science and Technology, China);*
Nils Hansen *(Sandia National Lab, USA)*

9:40 – 10:00 Coffee Break

10:00 – 12:00 **Group Discussion Session**: Identification of roadmap, challenges, & collaborations

Elementary Kinetics: Chair, **Robert S. Tranter**
(Argonne National Lab, USA)
Mechanism: Chairs, **Matt Oehlschlaeger**
(Rensselaer Polytechnic Institute, USA)
Flame Chemistry: Chairs, **Zheng Chen,**
(Peking University, China)
Timothy Ombrello
(Air Force Research Laboratory)

12:00 – 12:30 **Presentations of Group Discussion by Group Chairs**

Presentations and Workshop Summary

1. **Invited Presentations (11)**
2. **Workshop summaries (3)**
    - **Elementary Kinetics**
    - **Flame Chemistry**
    - **Mechanisms**
3. **Workshop presentation (8)**

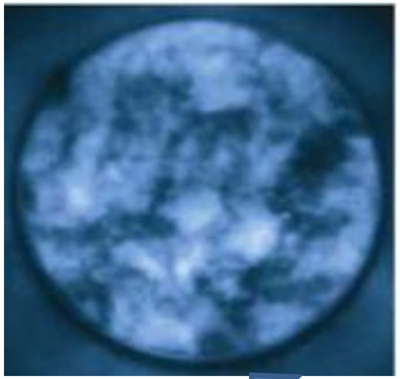
Laminar Flames and the Role of Chemistry and Transport

Yiguang Ju and **Sang Hee Won**
Princeton University, USA

Zheng Chen
Peking University, China

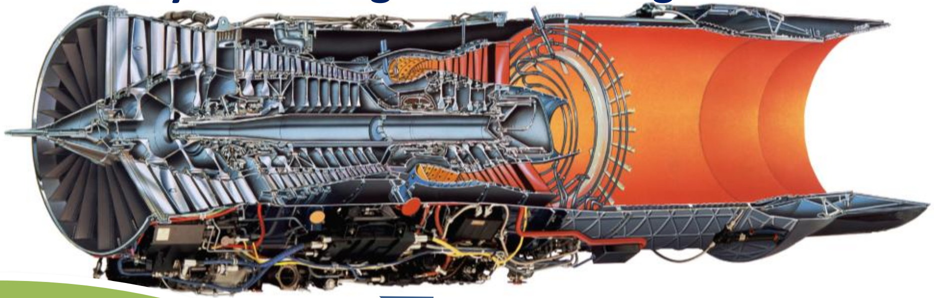
1st Flame Chemistry Workshop

Advanced Engines
require fuel flexibility and work near kinetic limit



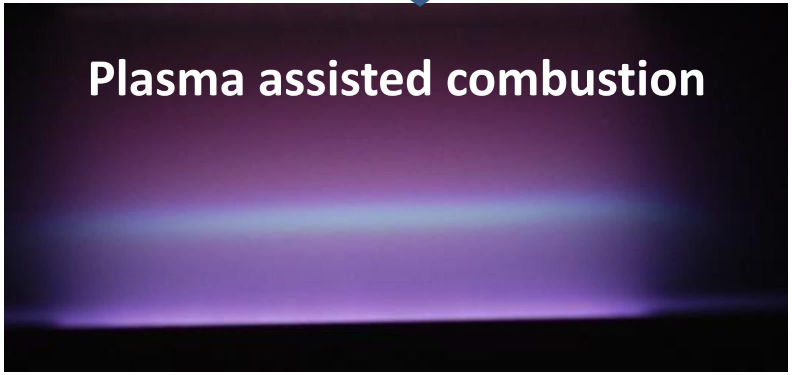
HCCI

Synfuels in gas turbine engine



- **Low temperature,**
- **High pressure,**
- **Near ign./ext . limit,**
- **Multiple fuels,**

Kinetic limiting



Plasma assisted combustion

“Validated“mechanisms?

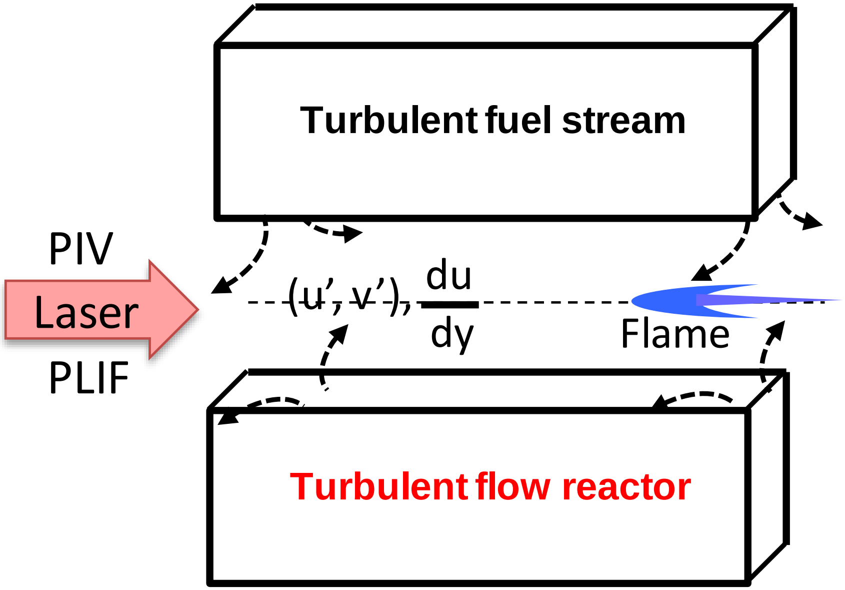
- Hundreds of fuels
- Different structures elements H, C, O, N, S…)
- Thousands species
- Extreme conditions

Two validation targets

- **Homogeneous ignition/reactor**
- **Inhomogeneous flames**

Flame regimes in combustion

How does chemistry affect flames?



Turbulent fuel stream

PIV

Laser

PLIF

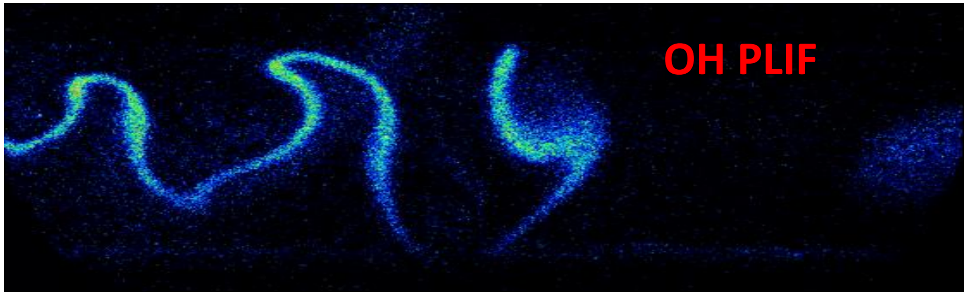
$(u', v'), \frac{du}{dy}$

Flame

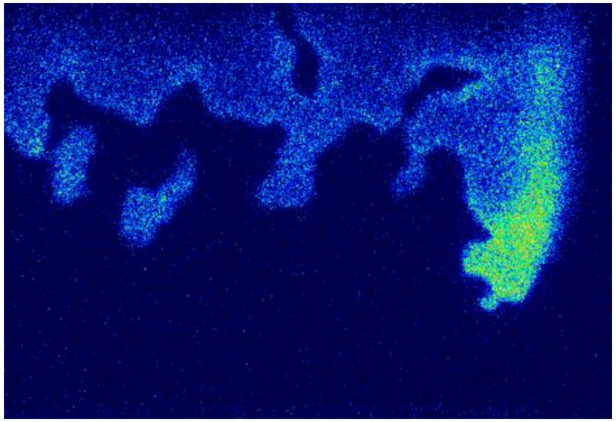
Turbulent flow reactor

Reactive flow

- **Thin flame**
- **Thickening flame**
- **Local extinction**
- **Re-ignition**



Propagating edge flame in a mixing layer

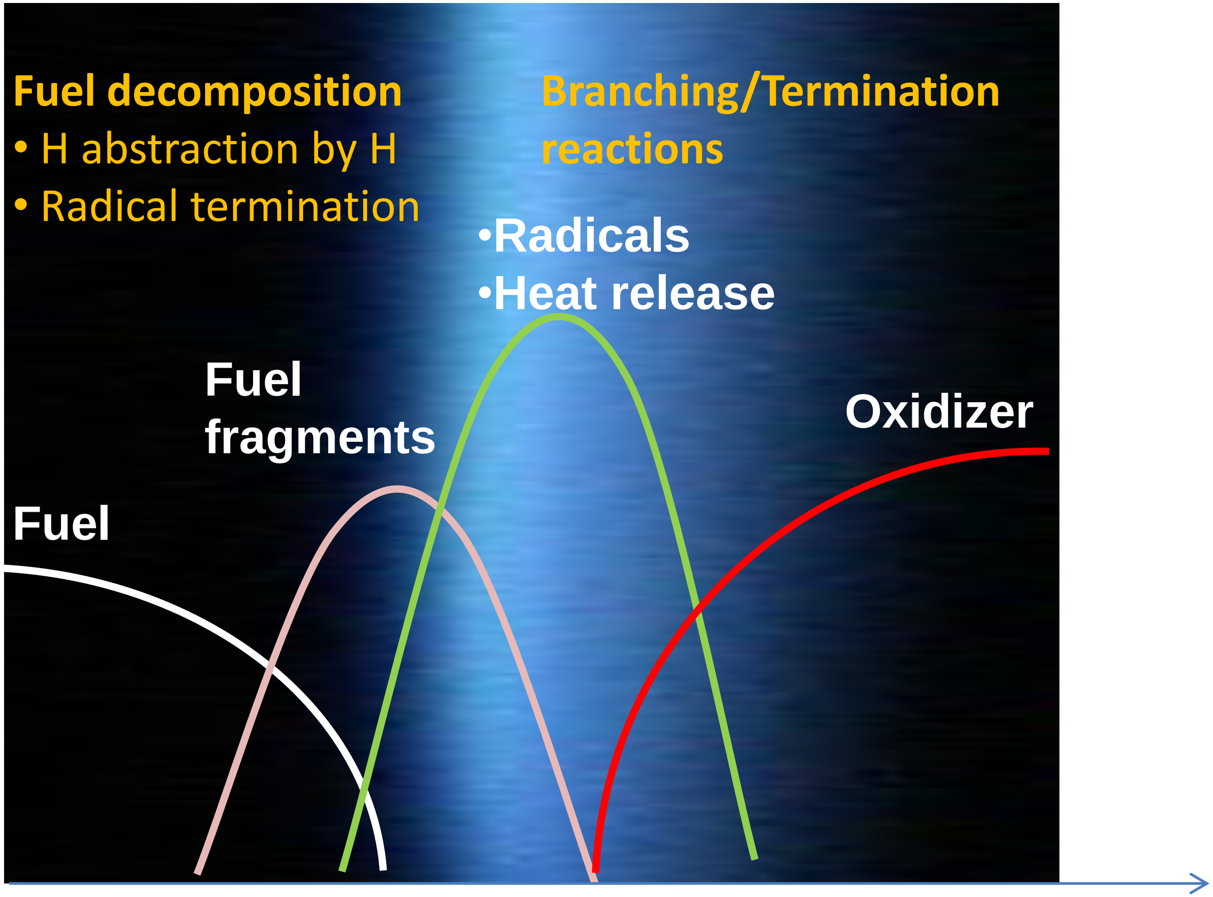


Premixed flame front

in non-uniform flow field with complex transport and chemistry coupling

Flames

- “Flame” is a ignition/reaction front supported by thermal and species transport



Fuel decomposition

- H abstraction by H
- Radical termination

Branching/Termination reactions

- **Radicals**
- **Heat release**

Diffusion
Fuel/Oxygen
Radicals/Fragments,
(e.g. H and C2H4)

Heat release rate
OH + CO =CO2 +H
HCO+OH= CO2+H2O

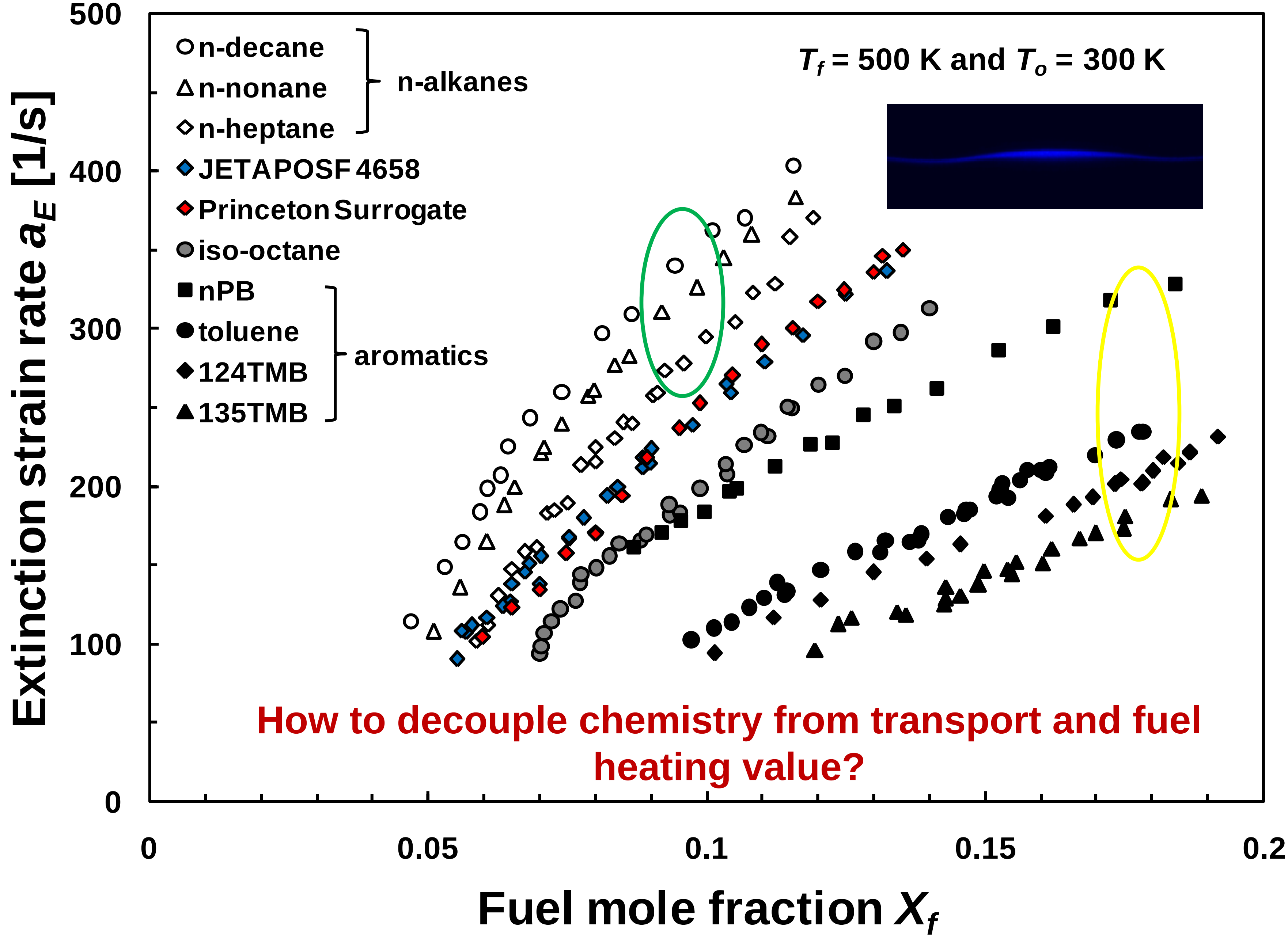
Non-uniform species/temperature distribution

1. Why is flame chemistry different from ignition?

- **Then, what is the role of transport on kinetics?**

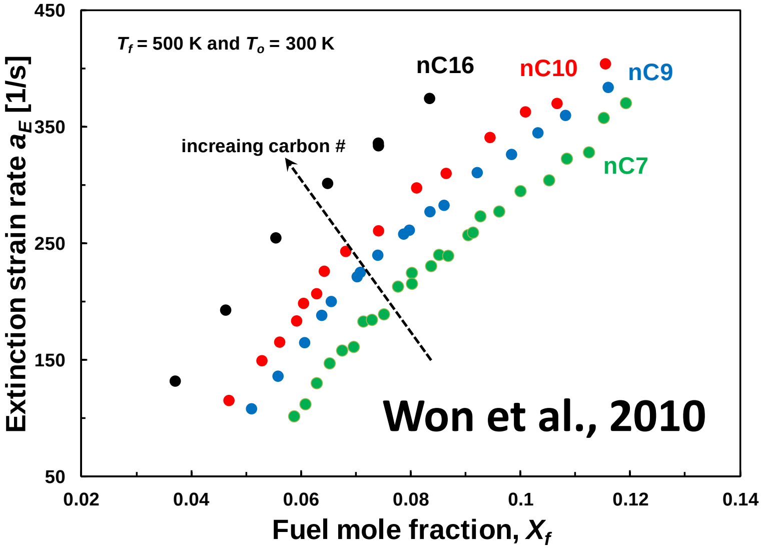
- **Is flame chemistry different from that of homogeneous ignition?**
- **How does transport and flame chemistry govern flame extinction?**
- **How does transport and flame chemistry affect unsteady flame initiation and propagation?**
- **How does low temperature chemistry change flame regimes?**

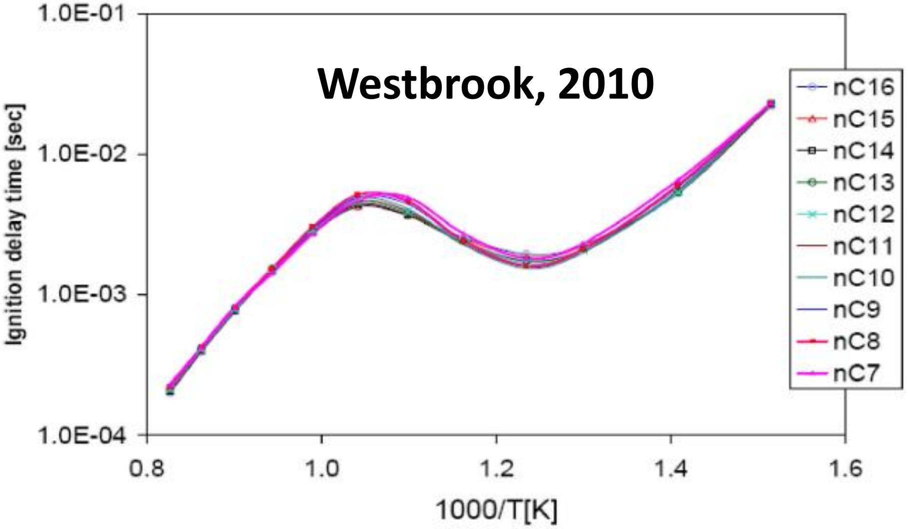
Flames: Different fuels have different extinction limits



How to decouple chemistry from transport and fuel heating value?

Ignition vs. flames: n-alkanes and esters





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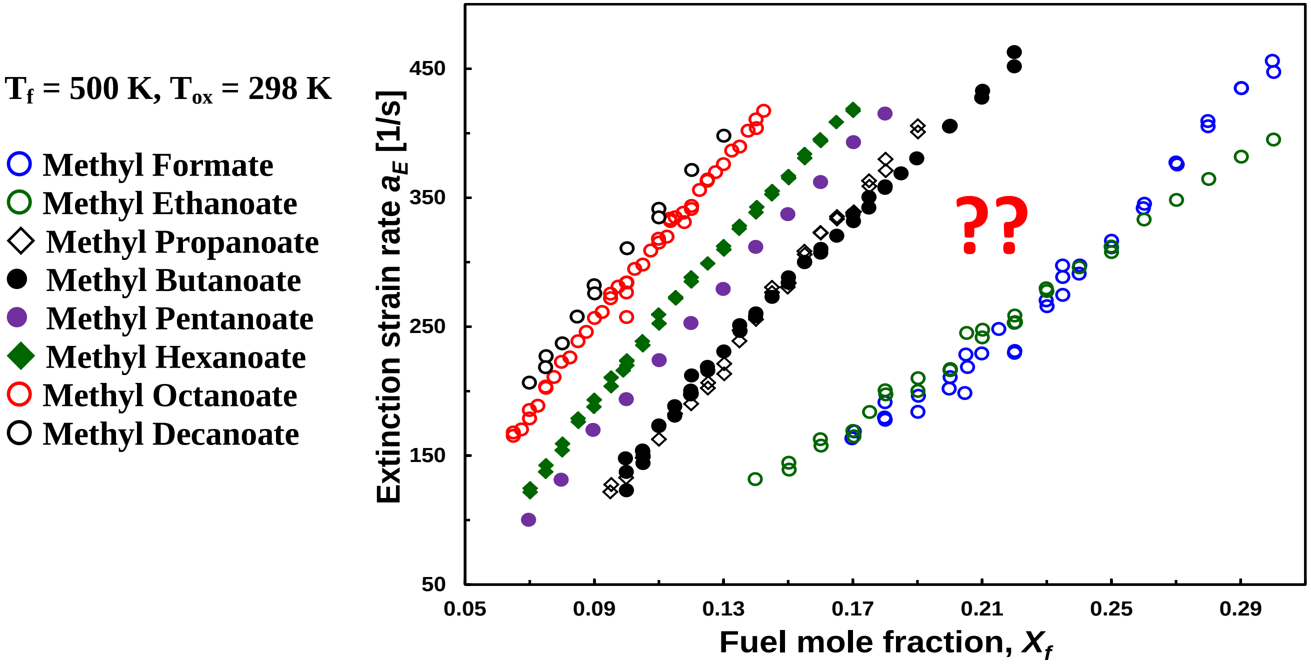
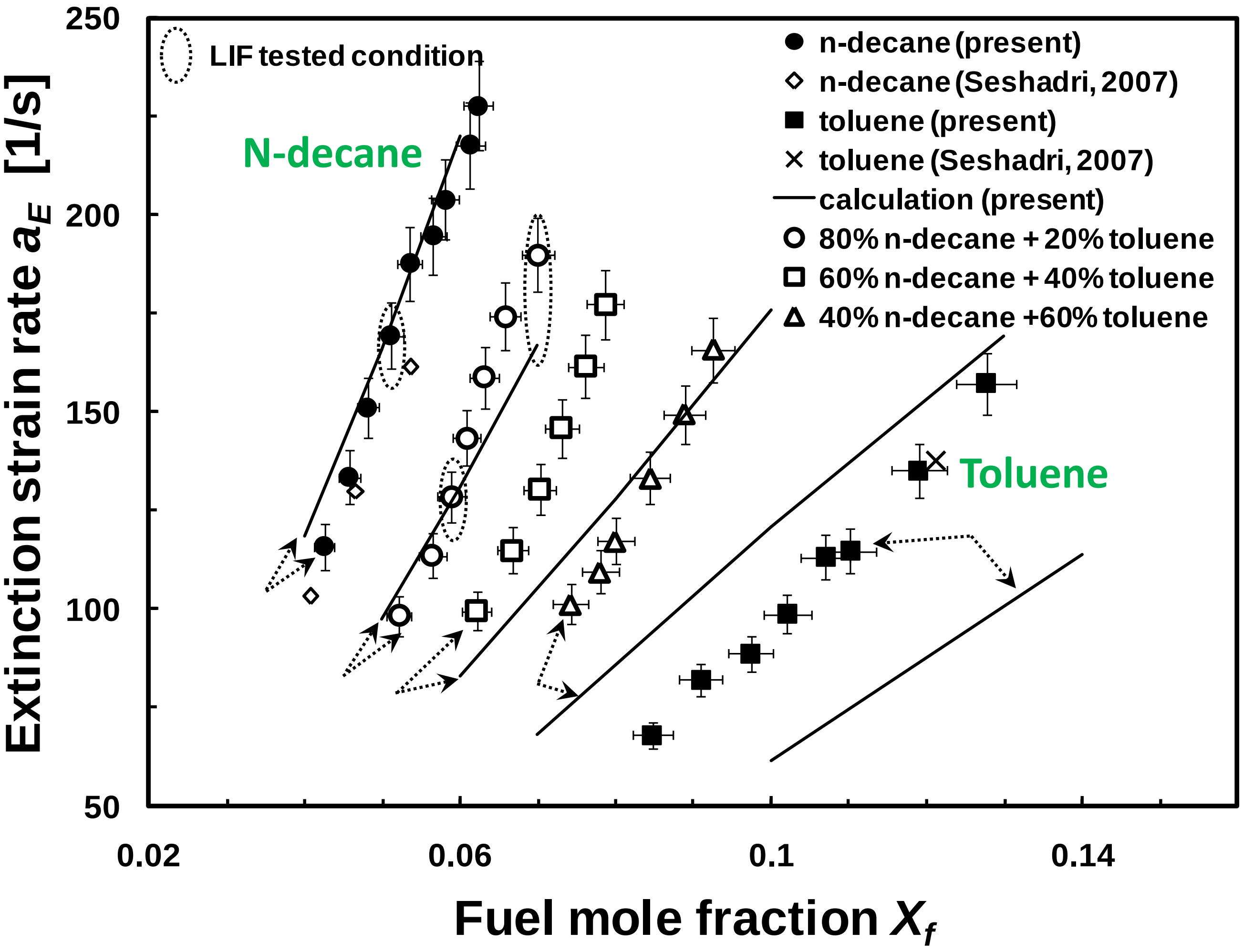


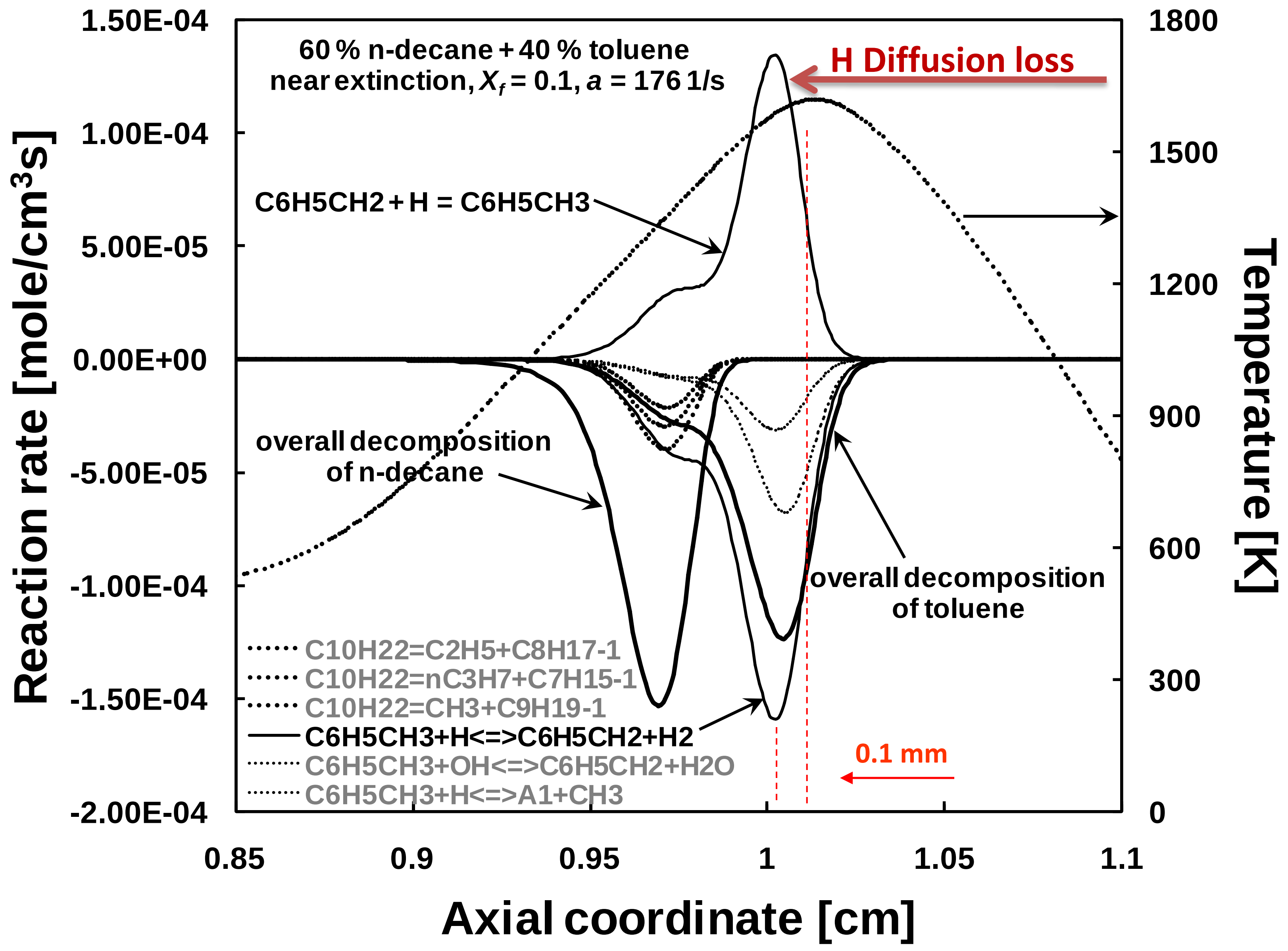
Kinetic coupling between alkanes and aromatics

Blending toluene into n-decane: Extinction Limits



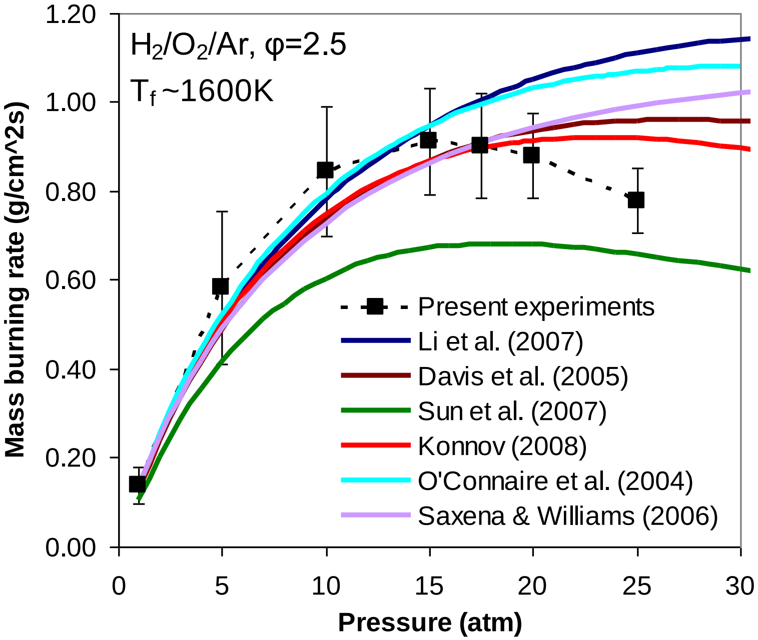
Won, Sun, Dooley, Dryer, and Ju, CF 2010

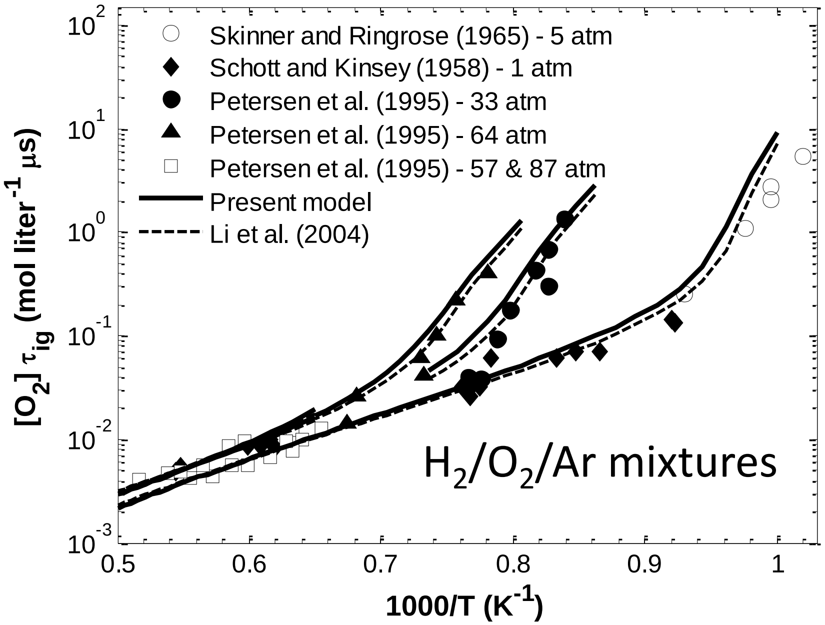
Kinetic coupling between n-decane and toluene in diffusion flames



Won, Sun, Dooley, Dryer, and Ju, CF 2010

High pressure hydrogen kinetics: ignition and flames





Uncertainty of HO2 related kinetics at high pressure,

- **Ignition governed more by chain initiation and branching rates**
- **Flames governed more by branching rate and heat release rate**
- **Different radical pool concentration (H, OH, …)**

Bulke, Marcos, Dryer, Ju, CF, 2010
Burke, Chaos, Ju, Dryer, Klippenstein, IJCK 2011

Difference of kinetics in homogeneous reactor and flames

Homogeneous reactor (800 K)

Fuel consumption by radicals

	% consumed by radical reaction			
component	OH	HO_2	H	O
n-decane	86%	6.0%	3.6%	2.0%
iso-octane	82%	6.5%	5.8%	2.3%
Toluene	88%		2.8%	4.5%

OH is r the most significant radical in fuel consumption

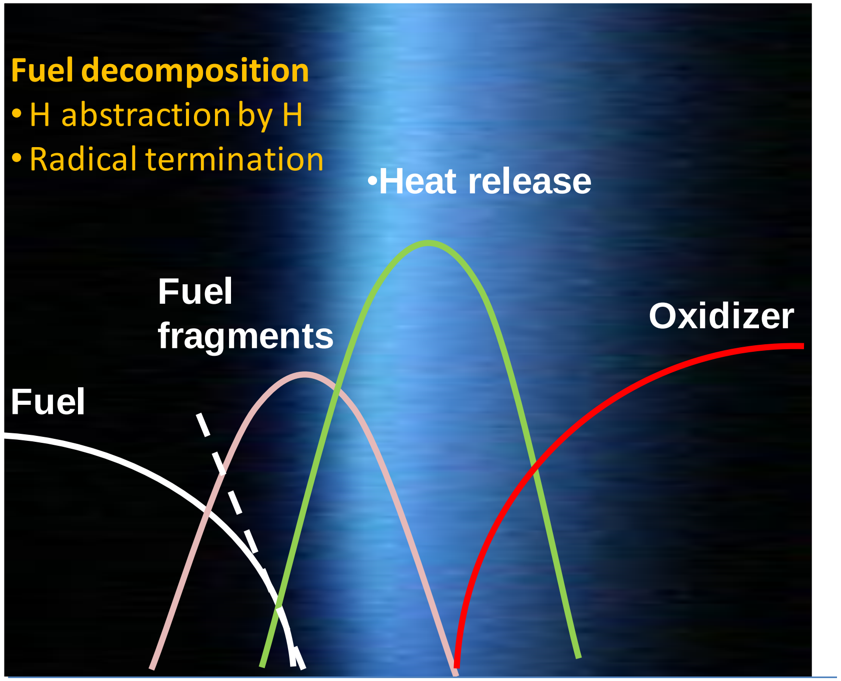
Diffusion flames (~1600K)

Fuel consumption by Radicals

component	**% by uni-molecular decomposition**	**% consumed by radical reaction**			
		H	OH	CH_3	O
n-decane [1]	19.3%	67.2%	6.1%	5.8%	0.1%
Methylbutanoate [2]	6.6%	70.8%	10.3%	8.1%	3.7%

1. Won et al. CNF 159 (2012)
2. Dooley et al. CNF 159 (2012) 1371-1384.

2. How does transport and flame chemistry govern diffusion flame extinction?



Fuel decomposition

- H abstraction by H
- Radical termination

- Heat release

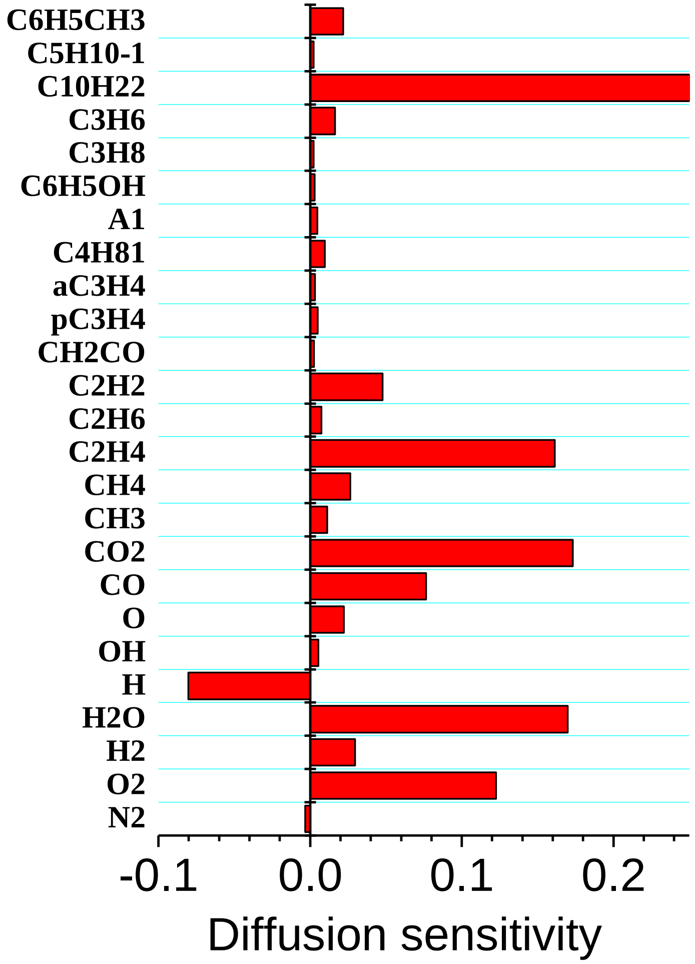
Fuel fragments

Fuel

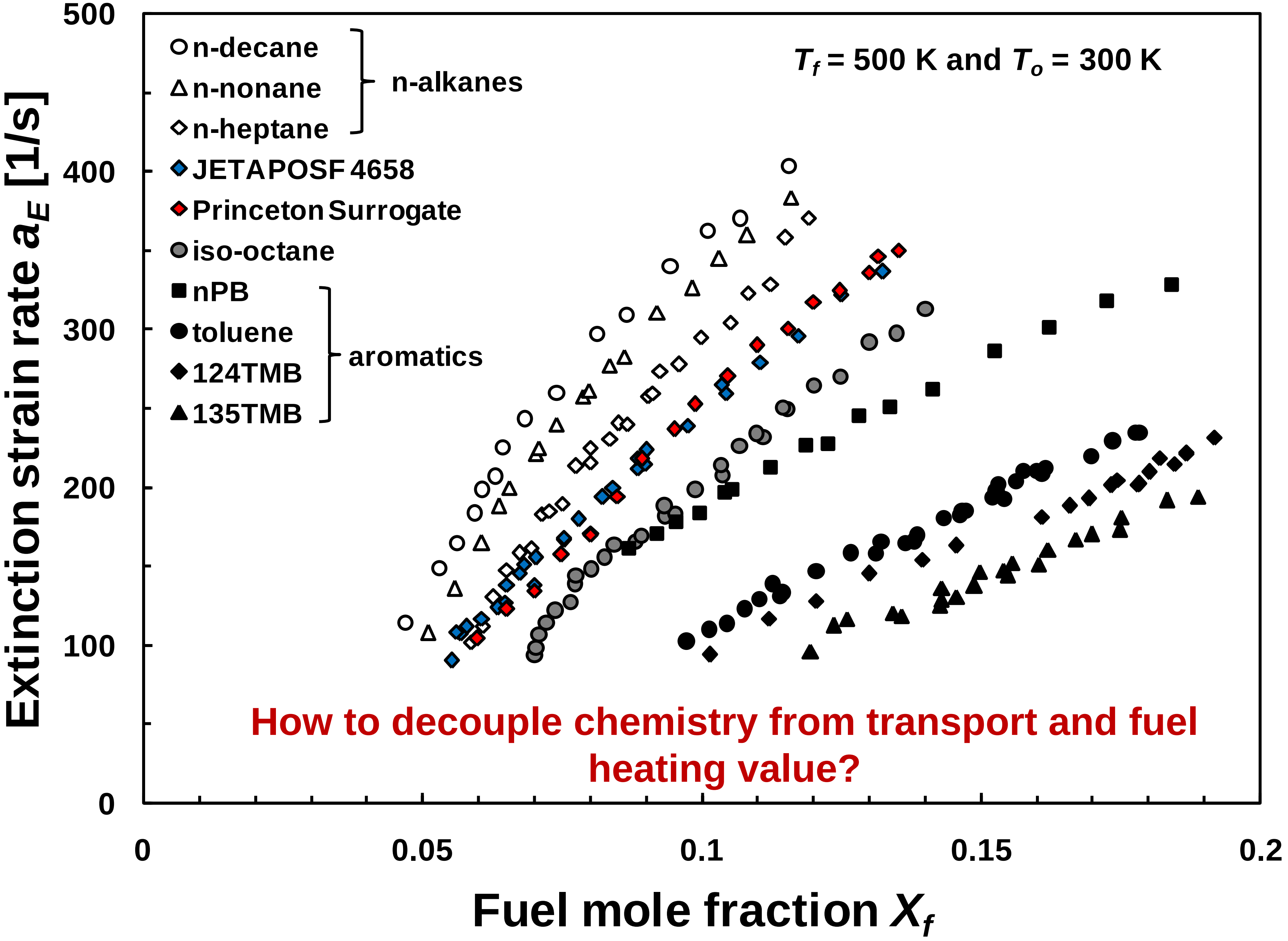
Oxidizer

$$Q \sim \rho D_i \frac{dY_F}{dx}\Big|_{0-}^{0+} = \int_0^{\delta} \omega_i dx$$

0.9N2+0.09n-decane+0.01toluene



Flames: Different fuels have different burning limits



How to decouple chemistry from transport and fuel heating value?

A generic correlation for extinction limit: Transport weighted Enthalpy & radical index

Theoretical analysis of Extinction Damkohler number

$$\frac{1}{Da_E} = \left[\frac{2}{e}\frac{\tilde{Y}_{O,\infty}}{\tilde{Y}_{F,-\infty}^{2}} Le_F^3 P(\eta_F, Le_F, Le_O) L(\eta_F, Le_F)\right]\left[\frac{1}{\tilde{T}_f - \tilde{T}_{-\infty}}\left(\frac{\tilde{T}_f^{\,2}}{\tilde{T}_a}\right)^3 \exp\left(-\frac{\tilde{T}_a}{\tilde{T}_f}\right)\right]$$

Extinction Strain Rate

$$a_e \propto \frac{1}{\sqrt{M_F/\overline{M}}}\frac{Y_{F,-\infty}Q_F}{C_p(T_f - T_{-\infty})} * R_i$$

Transport

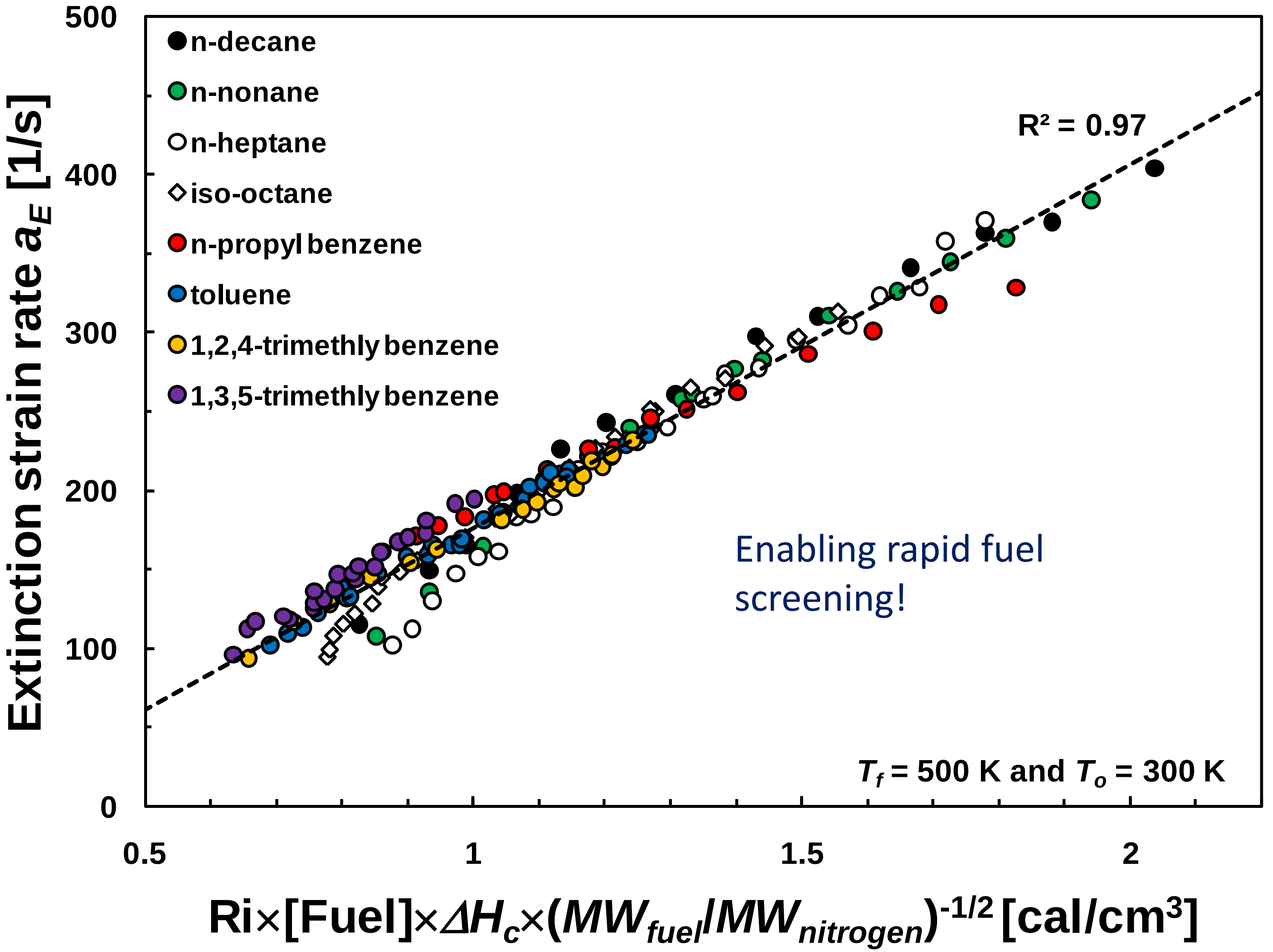
Heat release/heat loss

Fuel chemistry
Radical production rate

Transport weighted Enthalpy *Radical index

Won et al. CNF 159 (2012)

A General Correlation of Hydrocarbon Fuel Extinction vs. Transport Weighted Enthalpy (TWE) and Radical Index



Enabling rapid fuel screening!

TWE and radical index for predicting extinction limits and synfuel fuel ranking and screening

Radical Index

Representing radical pool

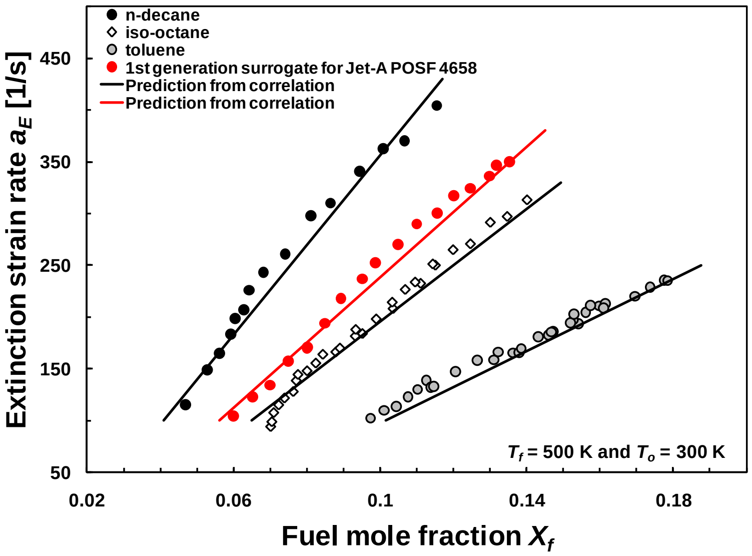
High temperature reactivity

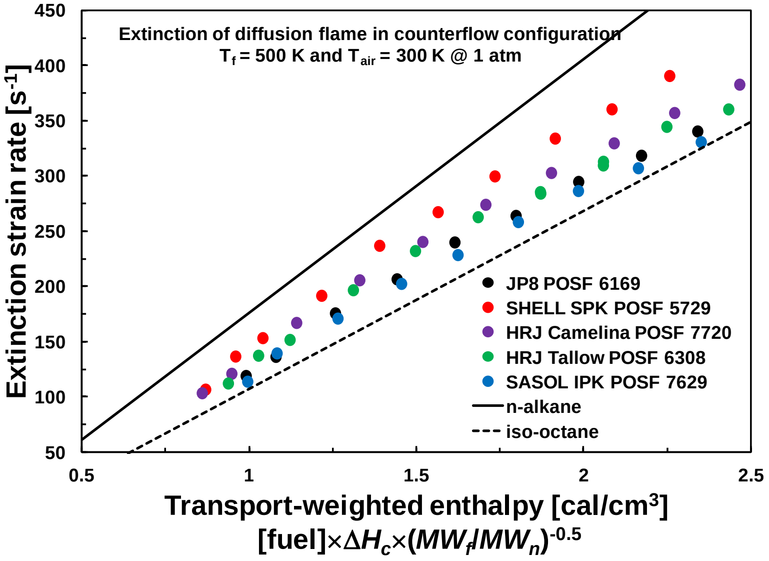
Fuel	Radical Index
n-dodecane	1.0
iso-octane	0.7
toluene	0.56
n-propyl benzene	0.67
1,2,4-trimethylbenzene	0.44
1,3,5-trimethylbenzene	0.36
JetA POSF 4658	0.79
S8 POSF 4734	0.86
JP8 POSF 6169	0.80
HRJ Camelina POSF 7720	0.82

Single fuel

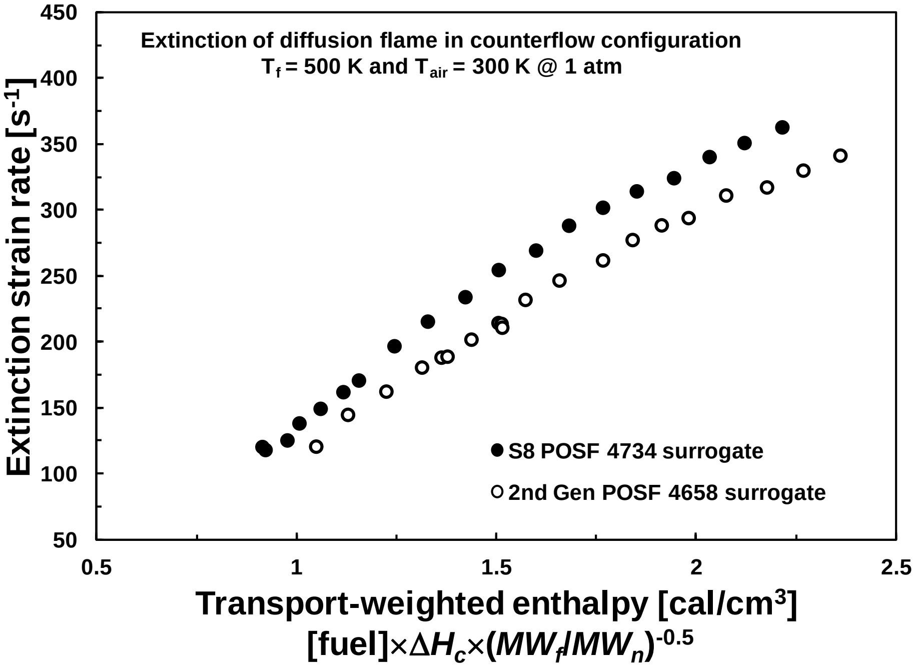
Real fuel

Synfuels

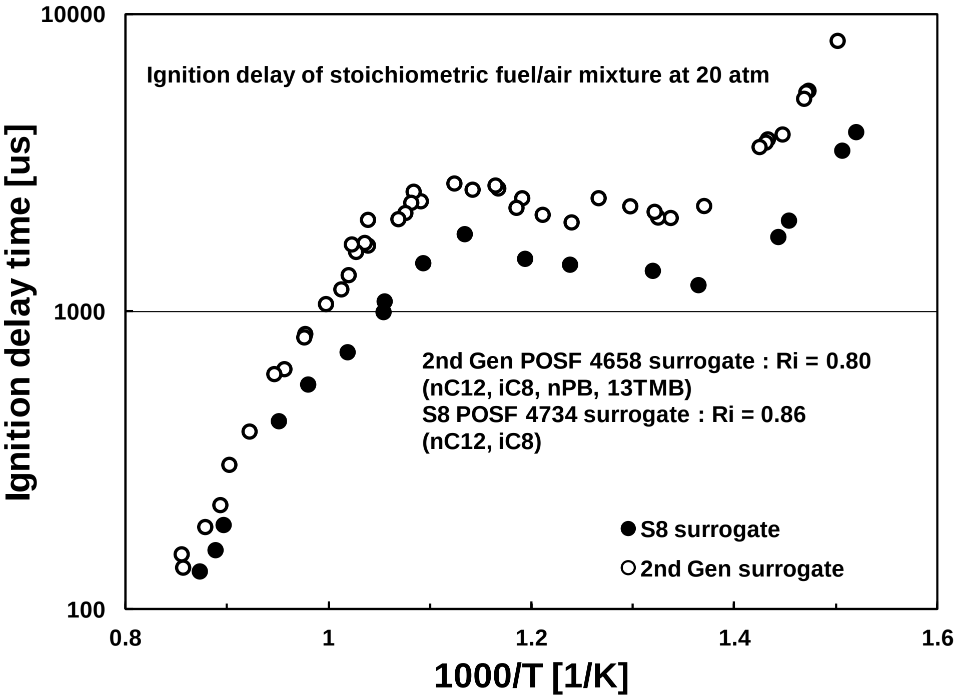




Ignition Delay vs. Radical Index (real fuel)



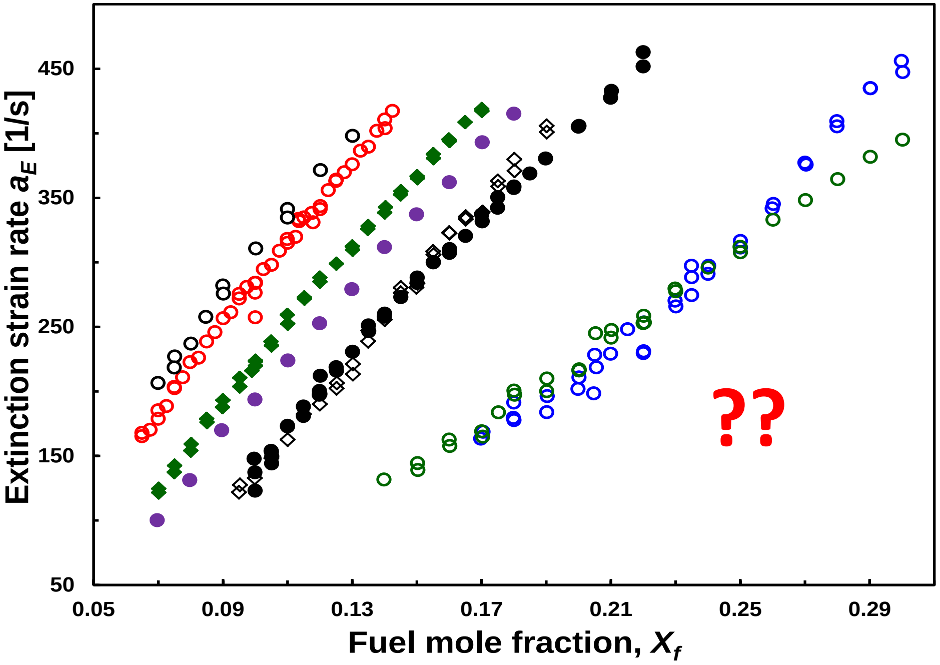
Dooley et al., CNF 159 (2012)



Consistent in high temperature reactivity

Measurements from RPI (Oehlschlaeger), Dooley et al., CNF 159 (2012), Dooley et al., CNF (2012) in press

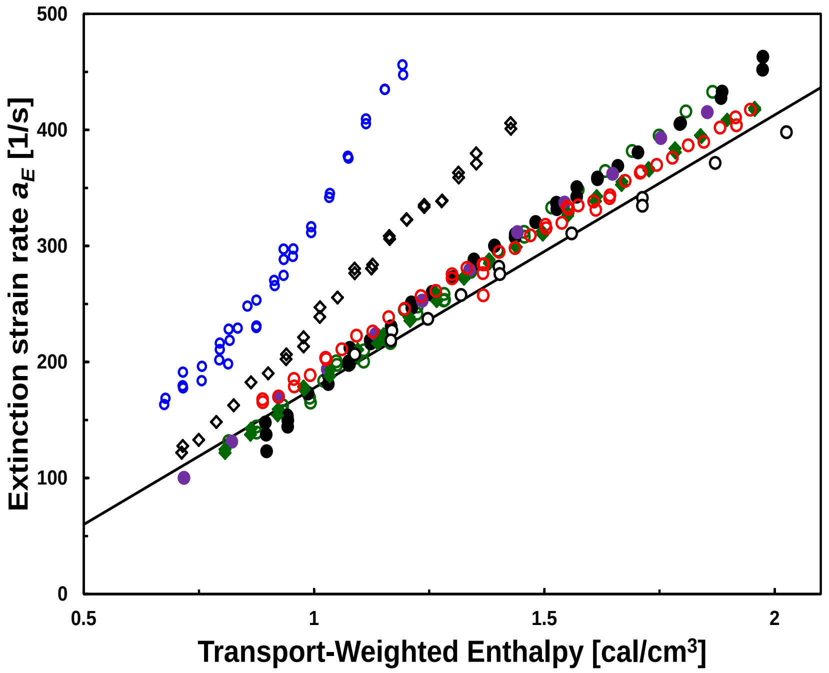
Scaling high temperature reactivity of methyl esters: Using TWE and Radical Index



T_f = 500 K, T_{ox} = 298 K

- ○ Methyl Formate
- ○ Methyl Ethanoate
- ◇ Methyl Propanoate
- ● Methyl Butanoate
- ● Methyl Pentanoate
- ◆ Methyl Hexanoate
- ○ Methyl Octanoate
- ○ Methyl Decanoate

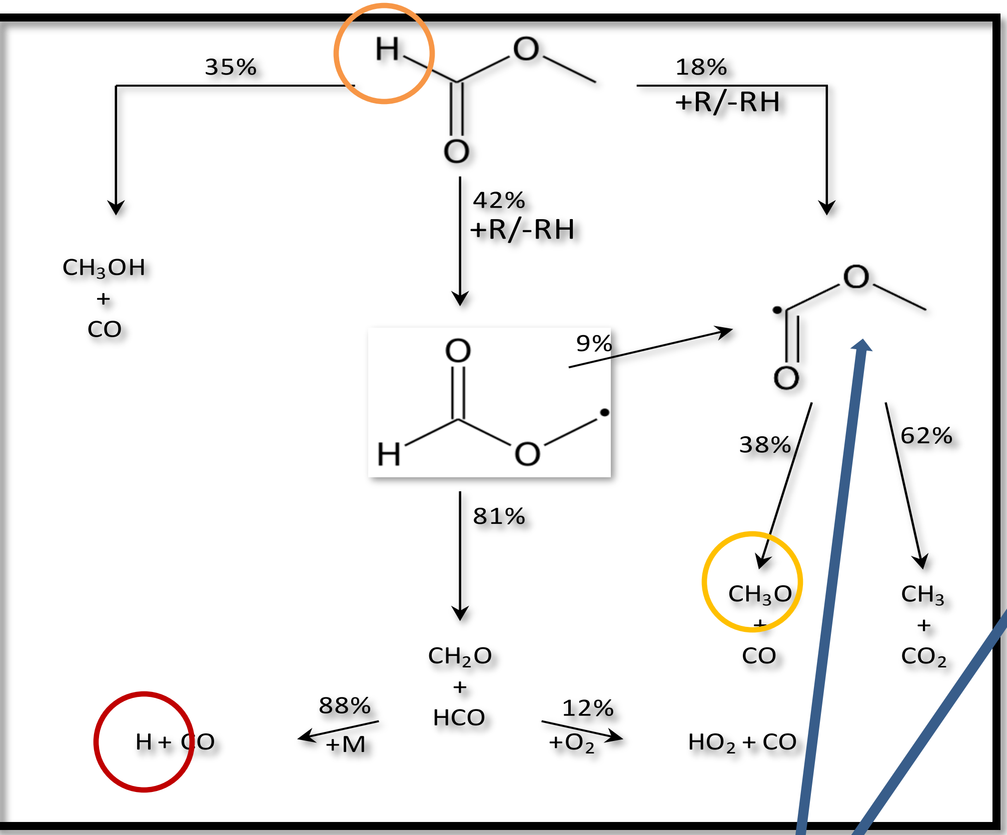
Different heating values
Transport properties



Diévart et al, 2012
to presented on Monday at 34th Symposium

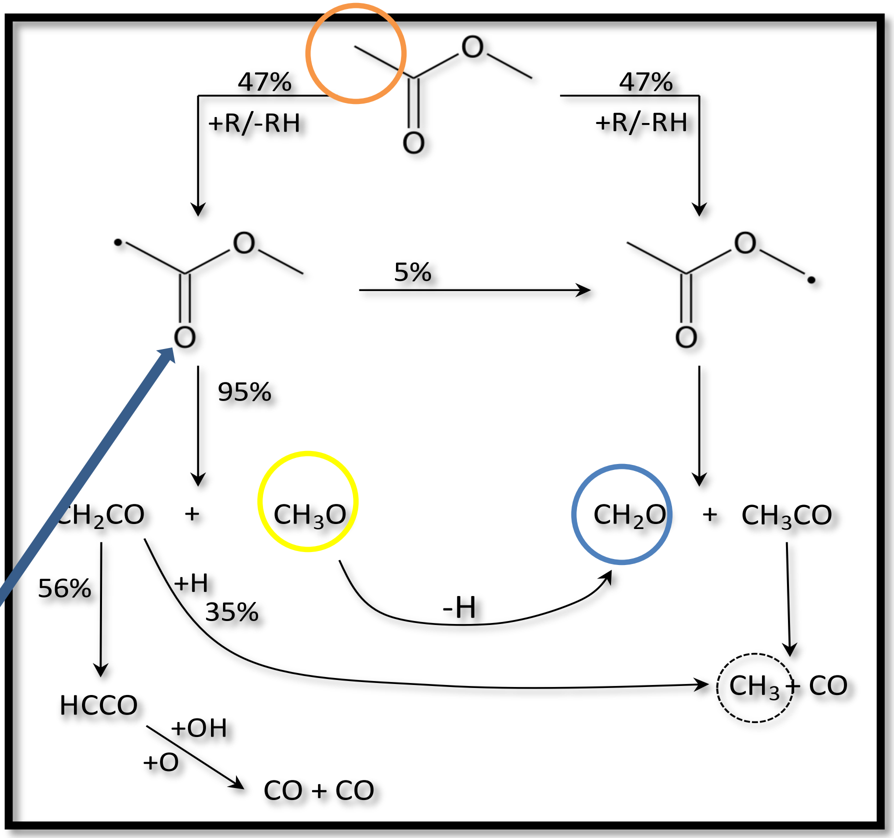
Impact of alkyl chain length on methyl ester reactivity

Methyl Formate, R0C


35%
H
O
O
18%
+R/-RH
42%
+R/-RH
CH_3OH + CO
9%
38%
62%
81%
CH_3O + CO
CH_3 + CO_2
CH_2O + HCO
88%
+M
H + CO
12%
+O_2
HO_2 + CO

Higher reactivity

Methyl Acetate, R1C


47%
+R/-RH
47%
+R/-RH
O
5%
95%
CH_2CO + CH_3O
CH_2O + CH_3CO
56%
+H
35%
-H
HCCO
+OH
+O
CO + CO
CH_3 + CO

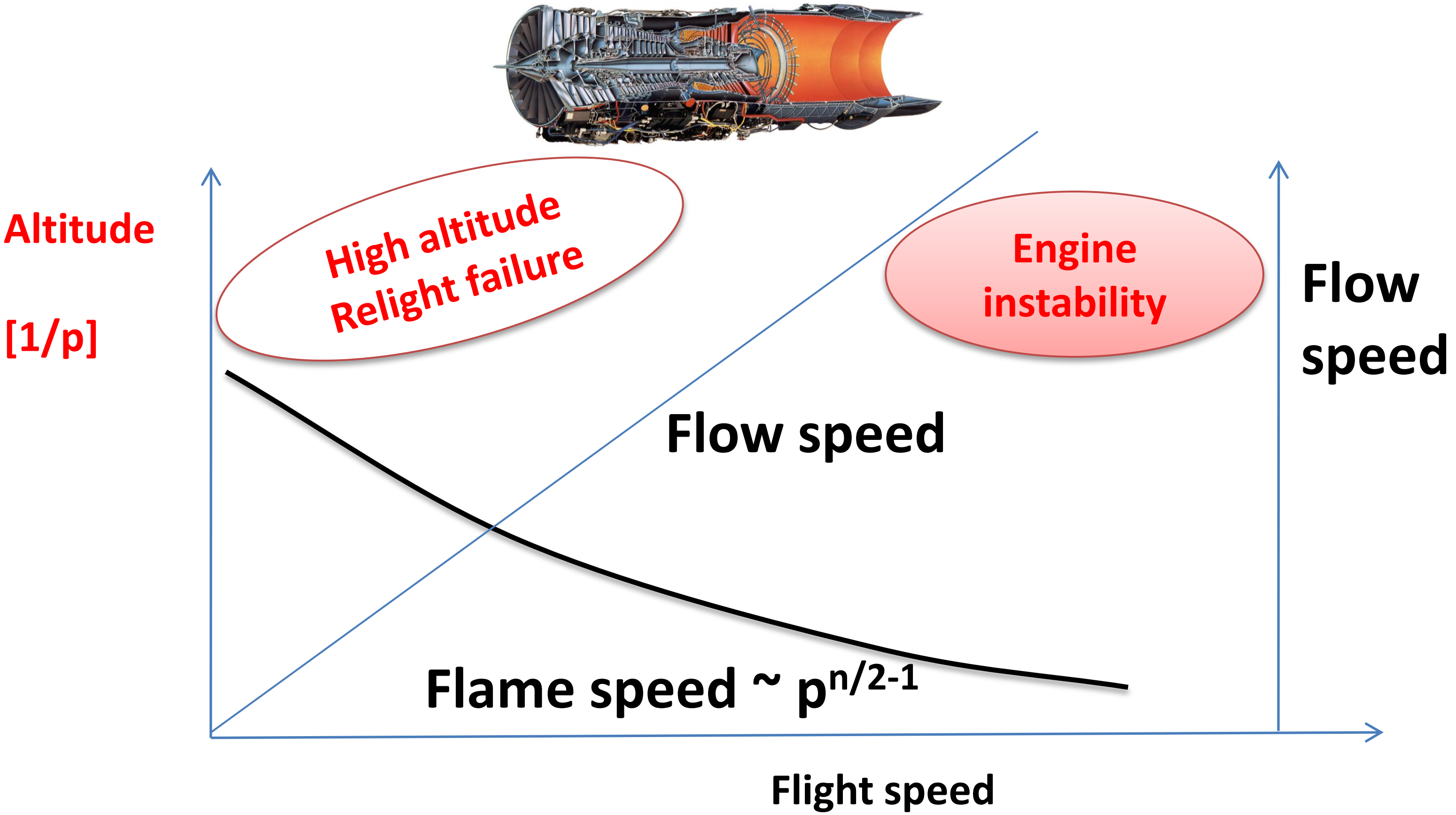
Lower reactivity

H abstraction reactions, CH3OCO and CH3OC(O)CH2 decomposition reaction rates: large discrepancies (Xueliang, 2012)

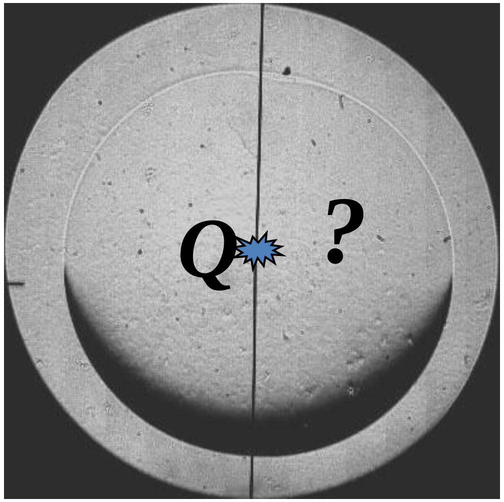
Diévart et al, 2012
to presented on Monday at 34th Symposium

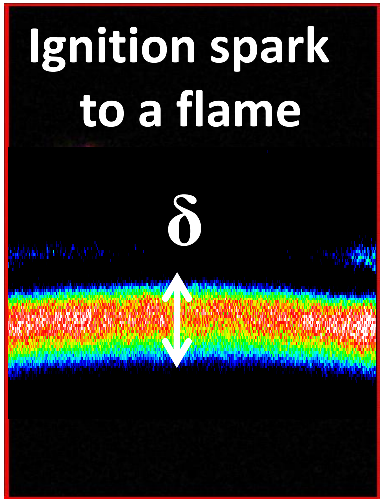
3. How does transport and flame chemistry affect flame initiation and propagation?

Puzzle of high altitude relight:
an unresolved ignition problem or a flame problem?



Is the flame speed really a problem for relight?





- **What governs the ignition & E_{ig}?**
- **What are the chemistry and transport effects?**

$$Le = \frac{\text{Thermal diffusivity}}{\text{Mass diffusivity}} = \frac{oxygen}{Jet\ \ fuel}$$

- **$E_{ig,min}$: Defined by flame thickness, δ (make a guess)?**

B. Lewis and Von Elbe (1961), Ronney, 2004, Glassman (2008)

$$E_{ig} = \frac{4}{3}\pi\delta^3\rho C_p(T_{ad} - T_\infty) \propto \frac{1}{S_u^{\ 3}} \propto \frac{1}{Le^{3/2}}$$

volume

heat capacity

Larger fuel molecules ⇔ smaller E_{ig}

- **$E_{ig,min}$: Defined by stable "flame ball" size?**

Zeldovich et al. (1985), Champion et al. (1986)

$$E_{ig} = \frac{4}{3}\pi R_Z^{\ 3}\rho C_p(T_{ad} - T_\infty) \sim Le$$

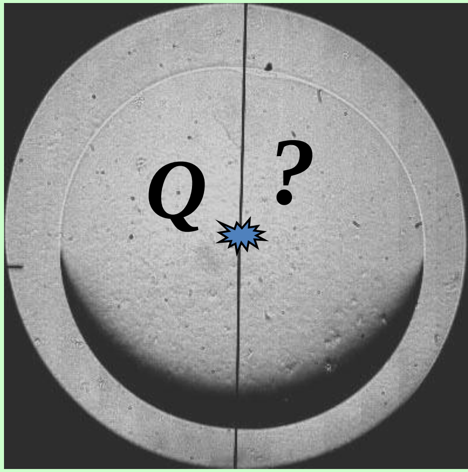
Larger fuel molecules ⇔ larger E_{ig}

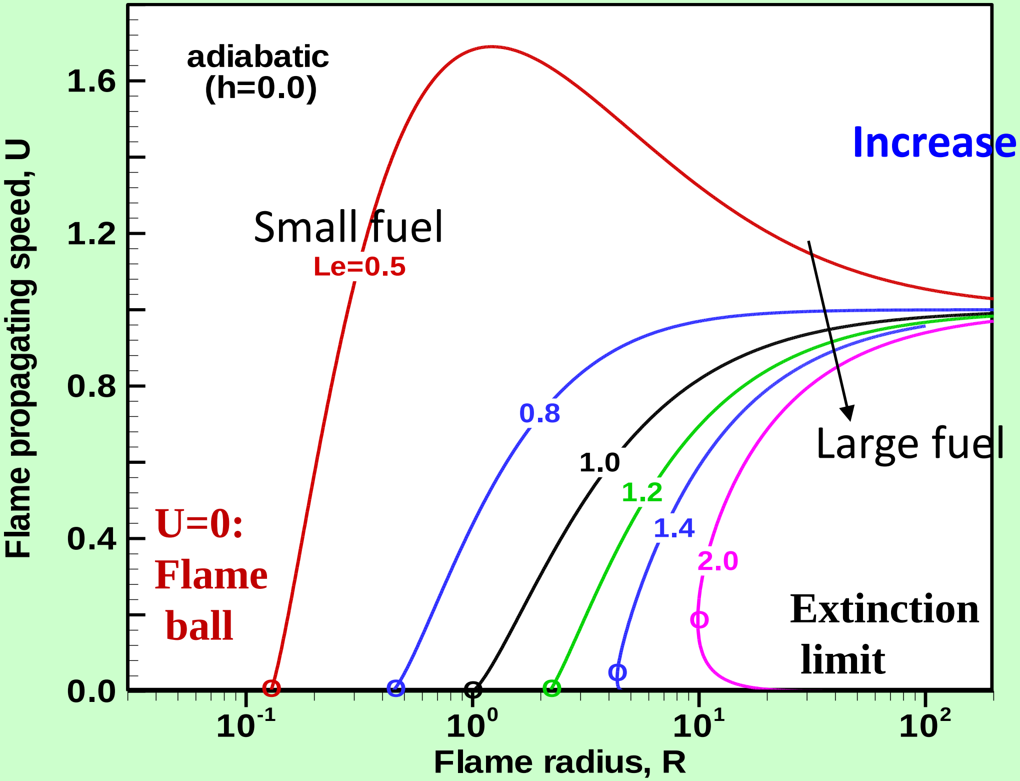
Theory: Critical Ignition Size vs. Flame Speed

Assumptions and simplification:

- **1D quasi-steady state, Constant properties**
- **One-step chemistry**
- **Center energy deposition**

$$T_f \cdot \frac{R^{-2}e^{-\mathrm{U}R}}{\int_R^{\infty} \tau^{-2}e^{-\mathrm{U}\tau}d\tau} - \mathrm{Q}\cdot R^{-2}e^{-\mathrm{U}R} = \frac{1}{\mathrm{Le}}\frac{R^{-2}e^{-\mathrm{ULe}R}}{\int_R^{\infty} \tau^{-2}e^{-\mathrm{ULe}\tau}d\tau} = \exp\left[\frac{Z}{2}\frac{T_f-1}{\sigma+(1-\sigma)T_f}\right]$$





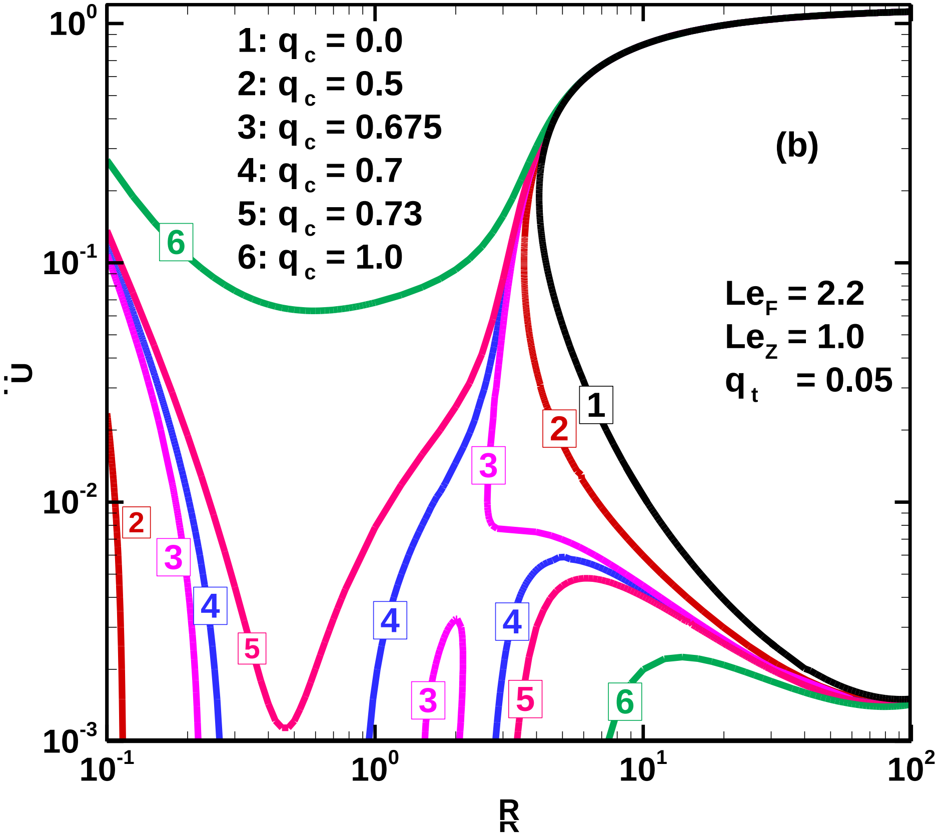
Increase of fuel molecule size

Chen & Ju, Comb. Theo. Modeling, 2007

The critical ignition size and energy is governed by two different length scales

- **Flame ball size (small Le)**
- **Extinction diameter (large Le)**

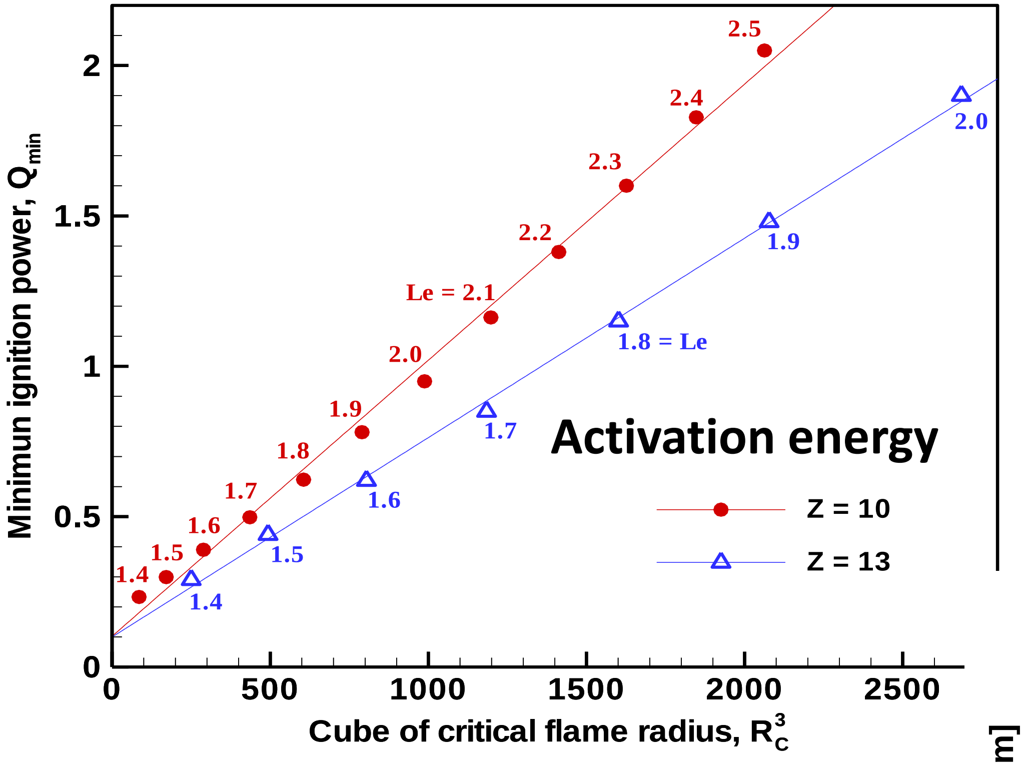
Ignition by heat and radical deposition (q_t=0.05)



LeF = 2.2

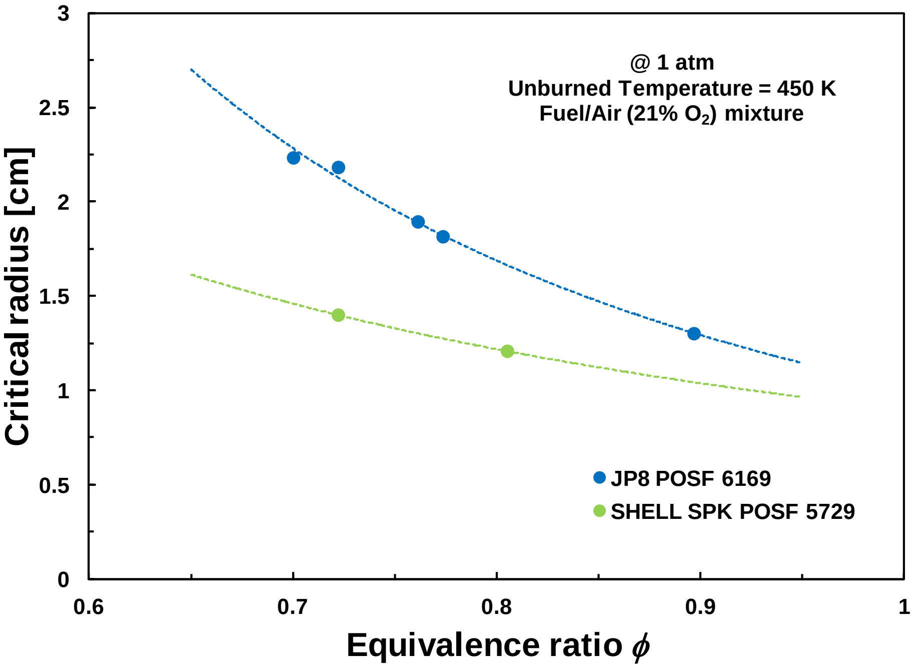
Chen et al. 2011

Ignition energy: impacts of flame chemistry and transport



Chen, Burke, Ju, Proc. Comb. Inst. Vol.33, 2010

Fuel	Mean molecular weight	Radical Index
JP8 POSF 6169	153.9	0.80
SHELL SPK POSF 5729	136.7	0.85

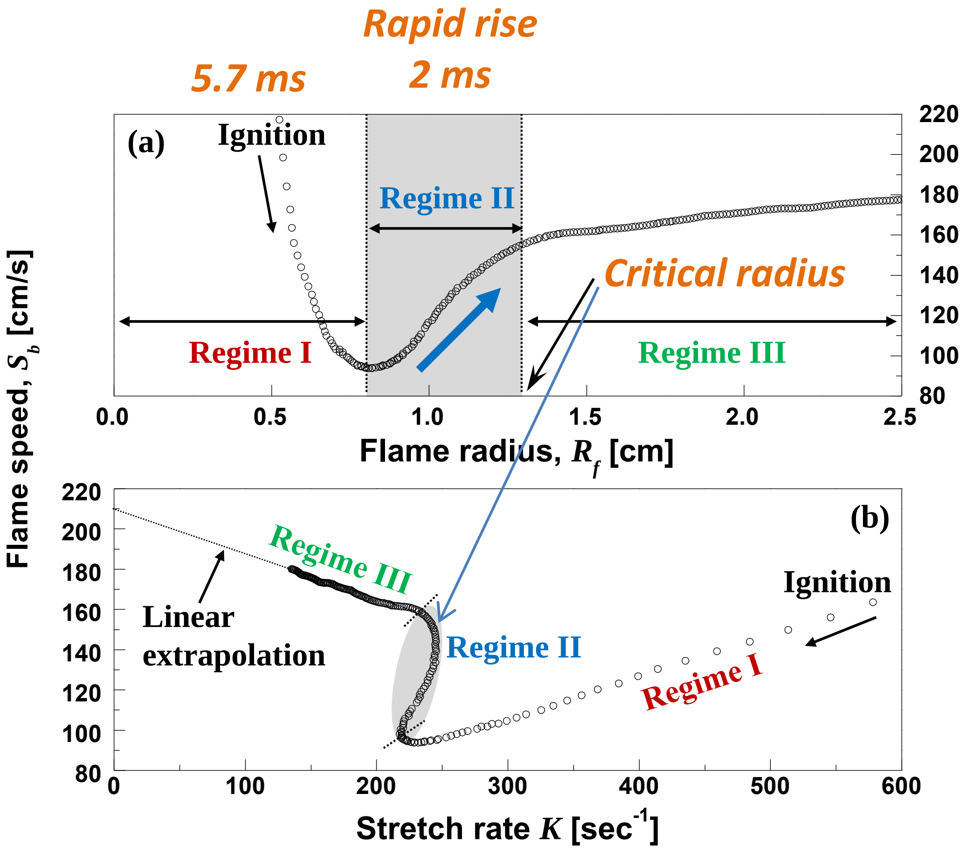


Won, Santer, Dryer, Ju, 2012

Unsteady flame initiation

Three different flame regimes (n-heptane/air)

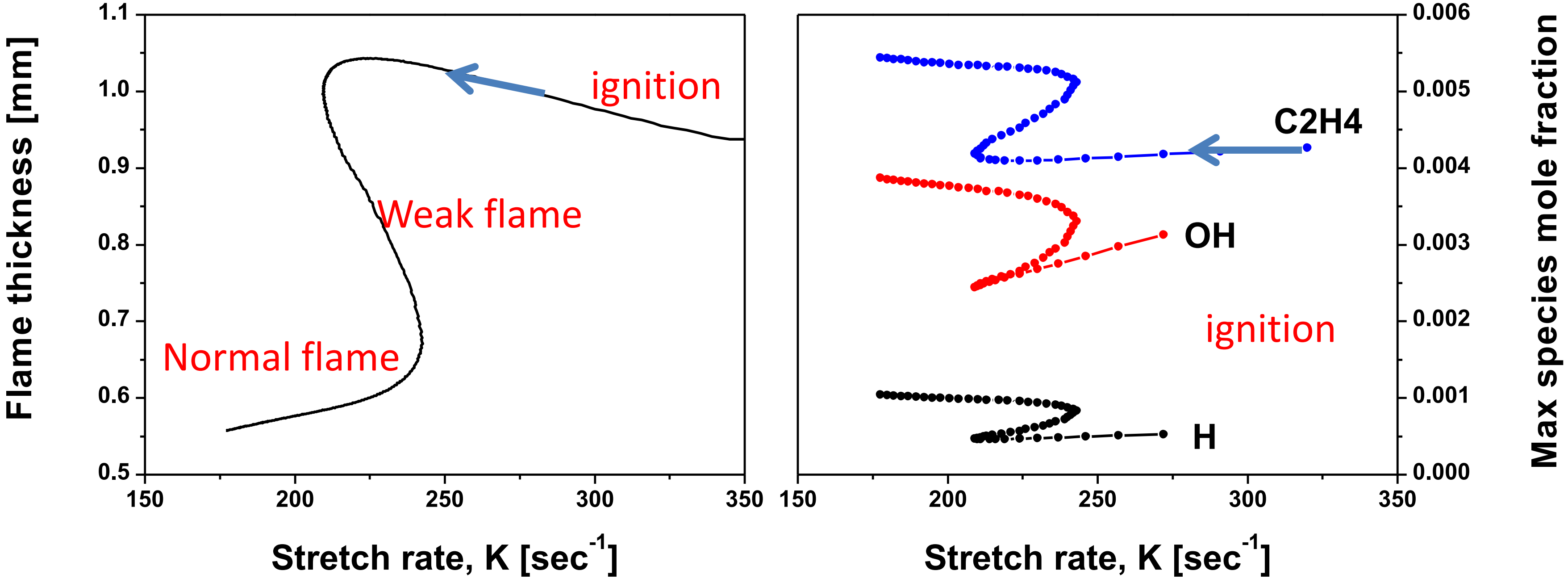
- **Regime I**
  - Spark assisted ignition kernel
- **Regime II**
  - Weak flame regime from sparked driven ignition kernel to normal flame
- **Regime III**
  - Self-sustained propagating normal flame



Kim et al, 2012, to be presented on Wednesday at 34th Symposium

Rapid change of flame structure in flame initiation process

(lean n-heptane/air)

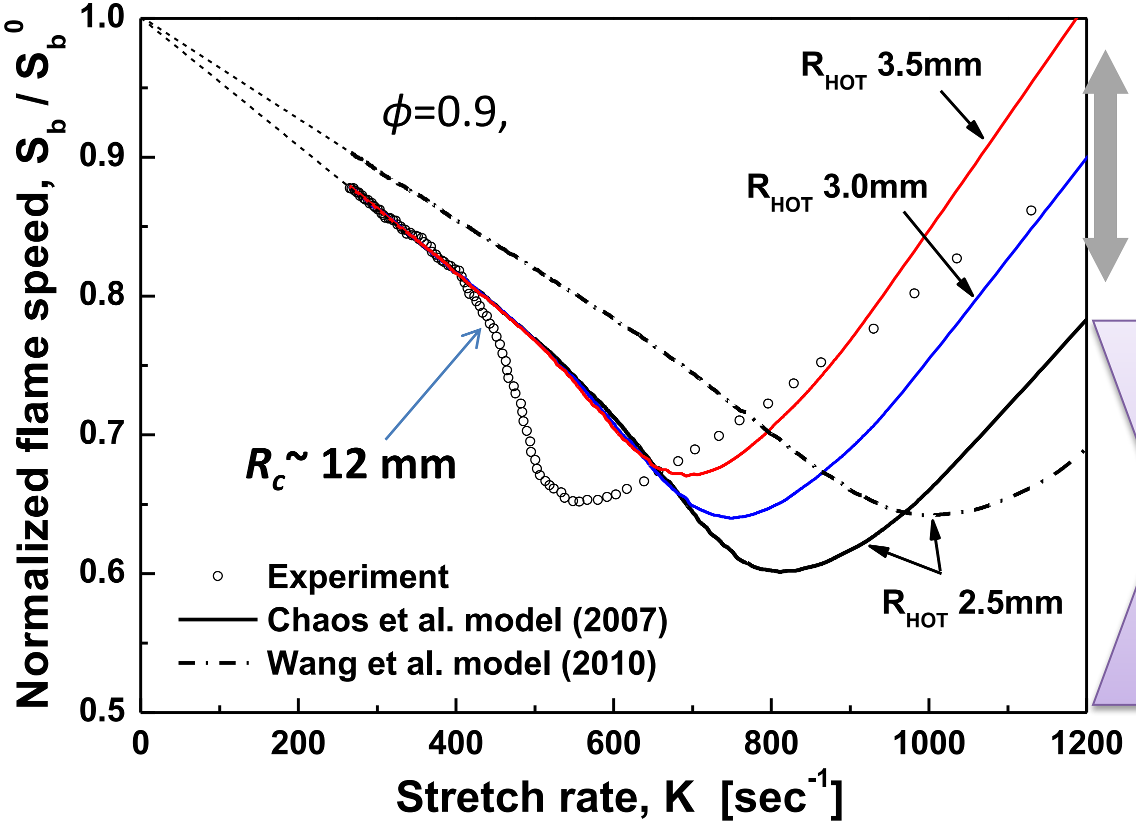


Completely different flame structures!

Kim et al, 2012, to be presented on Wednesday at 34th Symposium

Will a model for flame speed predict the unsteady flame initiation?

An example: Lean n-heptane flame initiation



Varying the Hot spot size

Accurate transient flame speed prediction

Turbulent modeling

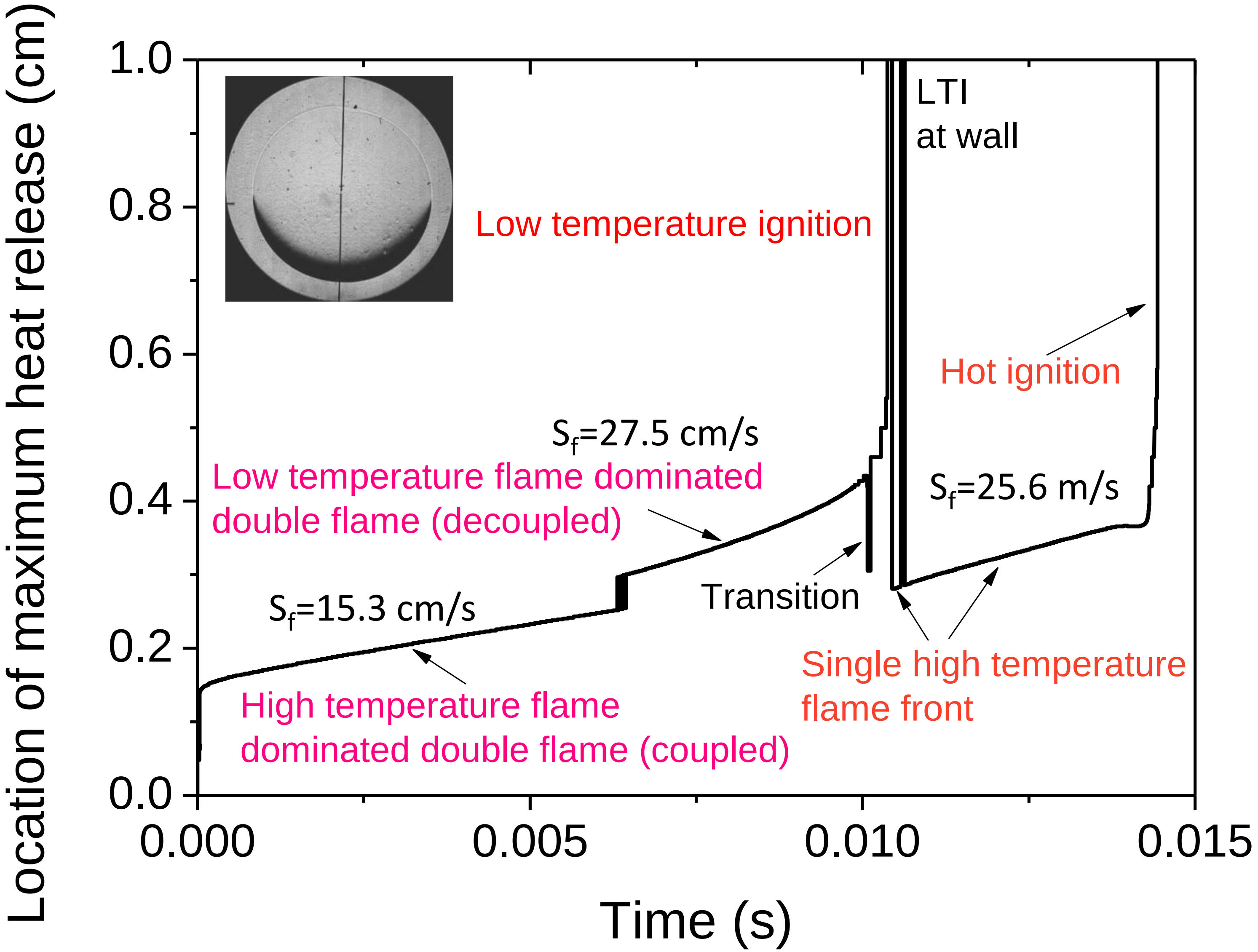
Critical flame initiation radius (R_c) >10 mm

4. How does low temperature flame chemistry affect flame initiation and propagation, and stabilization?

- Low temperature chemistry (multi-stage ignition)
- Plasma assisted low temperature ignition. extinction

Multi flame regimes in HCCI ignition n-heptane:40 atm, T=700 K

Movie

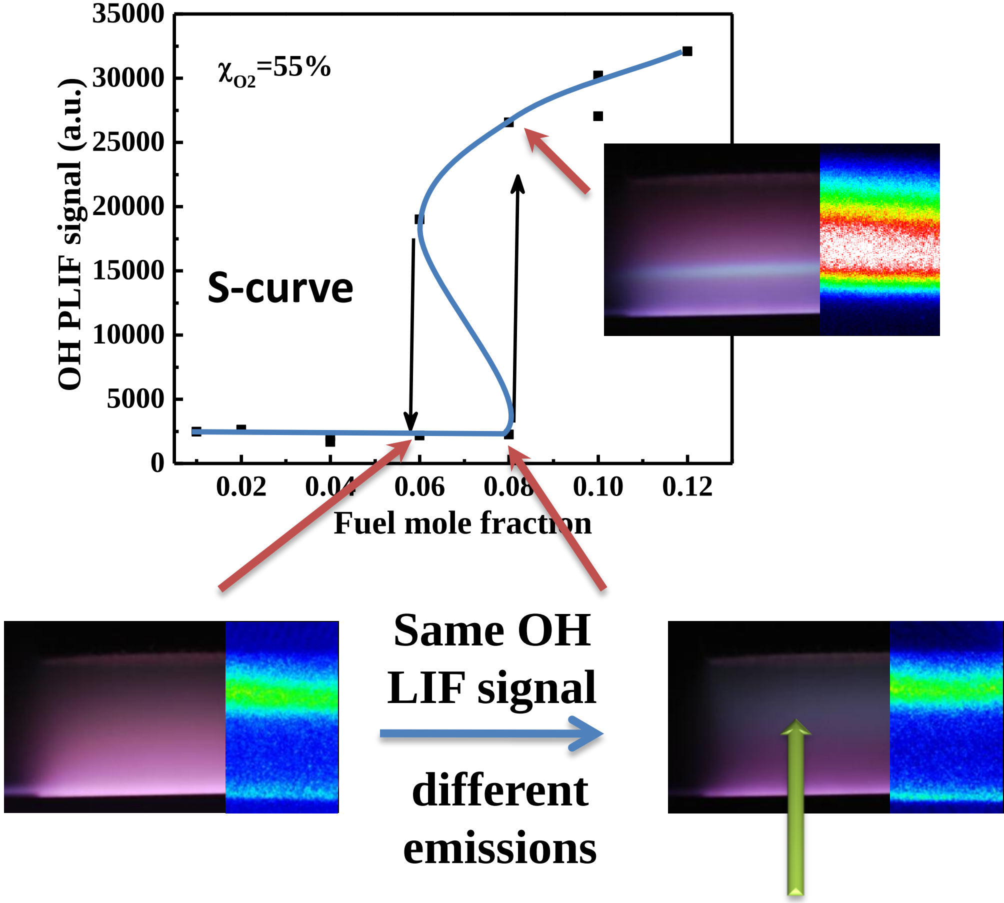


Ju et al. 33rd symposium 2011

New low temperature flame regime in Plasma assisted combustion

(Counterflow DME/O_2/He ignition)

Nano-sec discharge



Same OH LIF signal

different emissions

$CH_3O + OH \rightarrow CH_2O^* + H_2O$

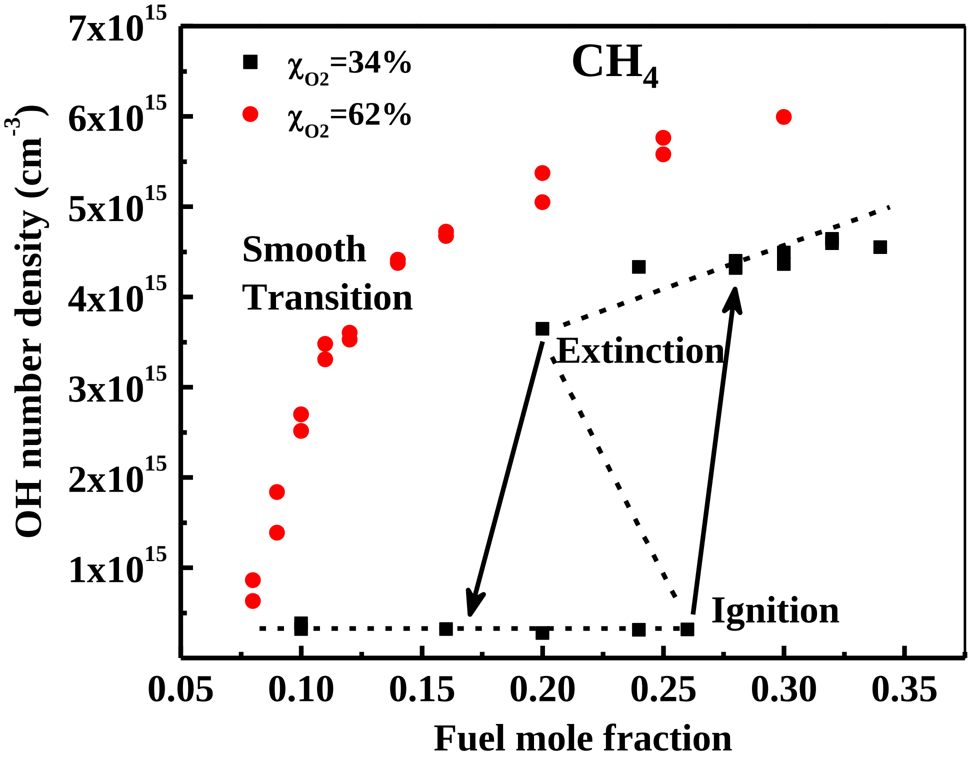
$RCH_2O + OH \rightarrow CH_2O^* + ROH$

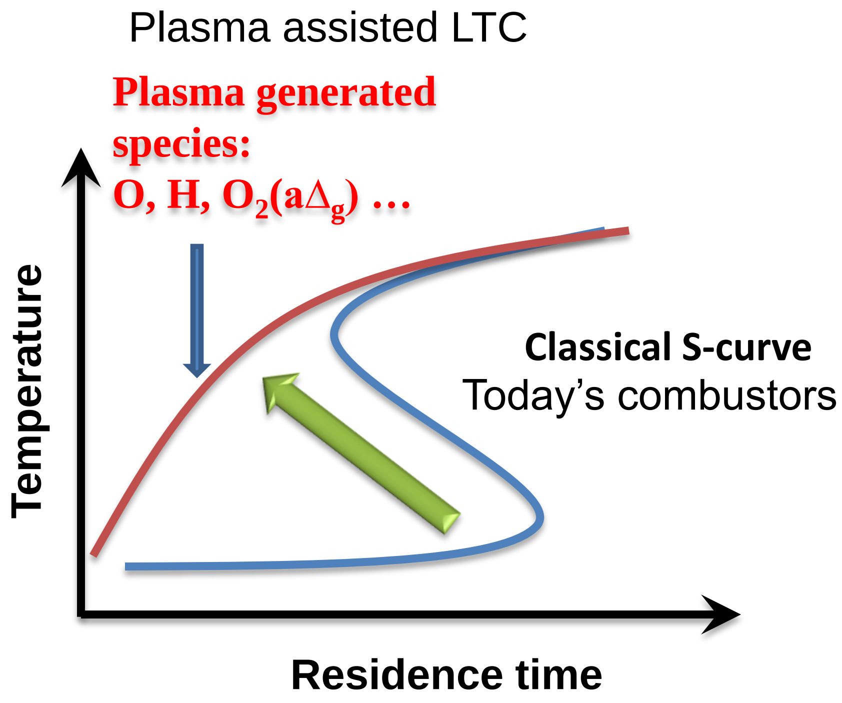
R: organic radicals

Sun et al., Friday 34th symposium on combustion, 2012

Kinetic enhancement of plasma assisted ignition: Change of S-curve

He/O_2 = 0.66:0.34 and 0.38:0.62 , P = 72 Torr, *f* = 24 kHz, a = 400 1/s




Plasma assisted LTC

Plasma generated species:
O, H, $O_2(a\Delta_g)$ …

Classical S-curve
Today's combustors

Sun et al., 34th symposium on combustion, 2012

Role of kinetics on PAC at low temperature?

Conclusion

- Flames chemistry differs from homogeneous ignition in diffusion, fuel decomposition, radical pool production/consumption.
- Low temperature and unsteady combustion processes lead to new different flame regimes and structures.
- Flame initiation and extinction are strongly affected by both transport and chemical kinetics.
- Transport weight enthalpy and radical index are developed for predicting extinction limit and ranking fuel reactivity
- Large uncertainties in elementary reaction rates of kinetic mechanisms for simple fuels exist in extreme conditions.
- A validated mechanism using flame speeds fails to predict unsteady flame transition and the critical flame radius.

Welcome to
The 1st International Flame Chemistry Workshop

Sincere Thanks To:

- Invited lecture (11) speakers and Session (4+1+2) chairs
- Committee and advisory board members
- All participants, especially poster (10) contributors
- Prof. TamásTurányi & Incoming Inc. for local organization

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Dr. Abate, Gregg (EOARD, AFOSR)
Dr. Li, Chiping (AFOSR)
Dr. Wells, Joe (ONRG)

Prof. Chung K. Law (CEFRC-Princeton)

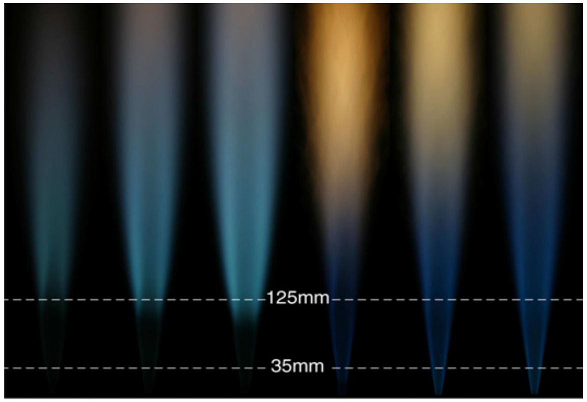
Turbulent Flames and the Role of Chemistry

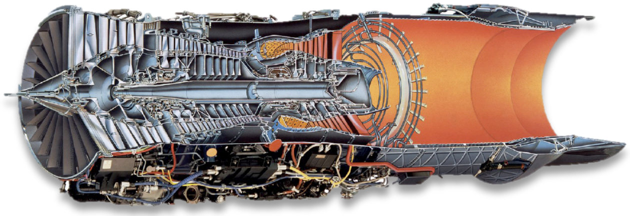
Matthias Ihme
Department of Aerospace Engineering
University of Michigan
Ann Arbor, MI 48109

Sponsor: ONR, AFOSR, DoE

Motivation

- Advanced combustion strategies rely on
  - Low/moderate temperature combustion
  - High-pressure operating conditions
  - (Ultra)Lean and stratified combustion
  - Emerging and alternative fuel combustion
- Challenges
  - Shift from mixing-controlled to kinetics-controlled combustion regime
    - Increasing relevance of ignition-kinetics and low-temperature chain-branching reactions
    - Increasing significance of turbulence and turbulence/chemistry interaction
    - Finite-rate chemistry effects
  - Operation near stability limit





Motivation

- Objective
  - Development of high-fidelity combustion for prediction of turbulent reacting flows under consideration of
    - Finite-rate chemistry
    - Turbulence/chemistry coupling
    - Transient combustion-dynamical processes
- Relevance
  - Identify and isolate combustion-physical processes
  - Combustor-design, control, and optimization
  - Guide experimental instrumentation

Overview

- Motivation
- LES-combustion modeling
  - Flamelet-based formulation
- ***Part 1:*** Modeling and simulation of combustion-physical processes: LES of lifted vitiated flames
- ***Part 2:*** Guide experimental instrumentation: Turbulent inhomogeneities and facility-effects?
- Summary and conclusions

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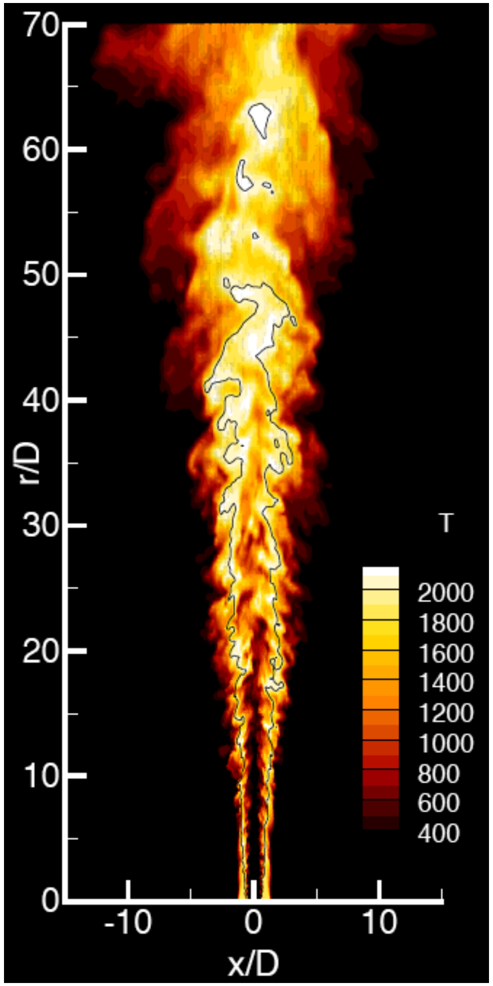
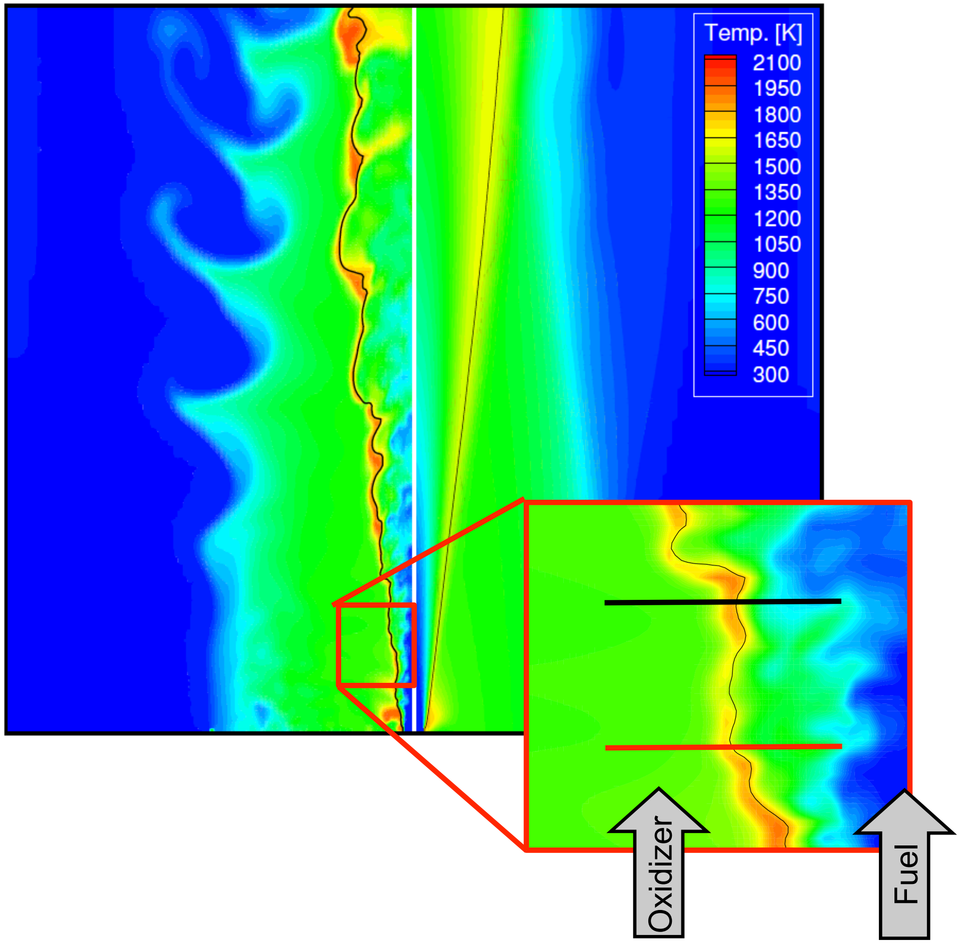
LES Combustion Modeling

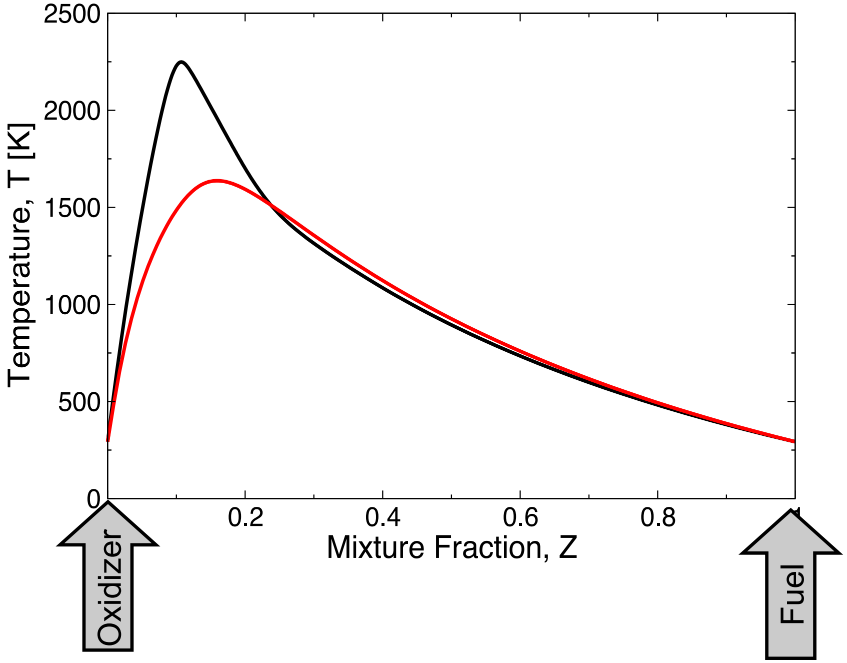
- LES Flamelet-based combustion models
  - Representation of turbulent flame as unsteady reaction-diffusion layer that is embedded in turbulent flame
  - Interaction of flame structure with turbulent environment leads to stretching, deformation, and extinction of flame



LES Combustion Modeling

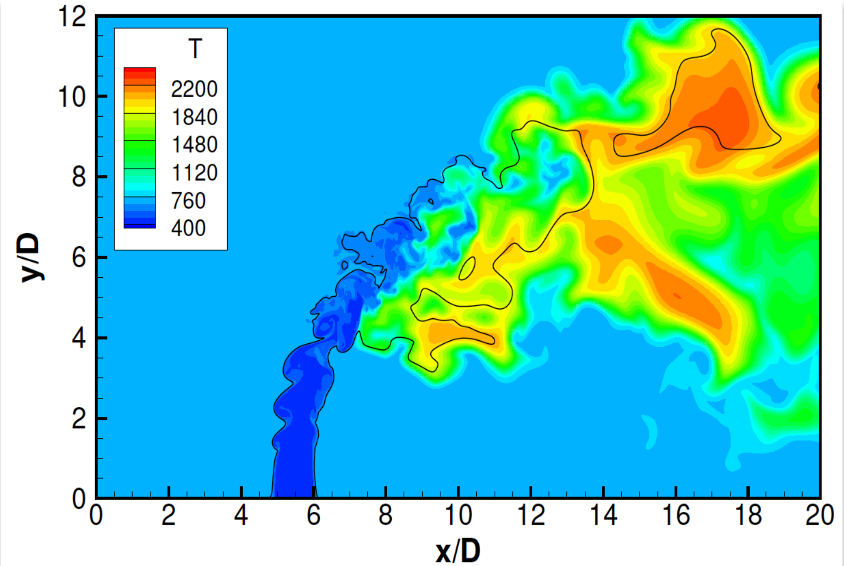
- LES flamelet-based combustion model

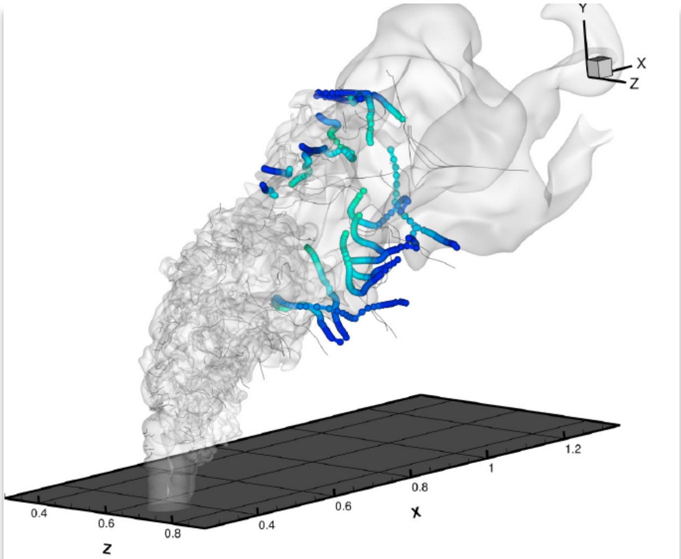




LES Combustion Modeling

- Flamelet-structure in turbulent reacting flows
  - Analysis Tools: DNS-database[1] of reacting jet-in-cross-flow
    - Fuel: N2-diluted H2-jet, 350 K
    - Oxidizer: Air, 750 K
- Extract instantaneous local flamelet structure from DNS-database





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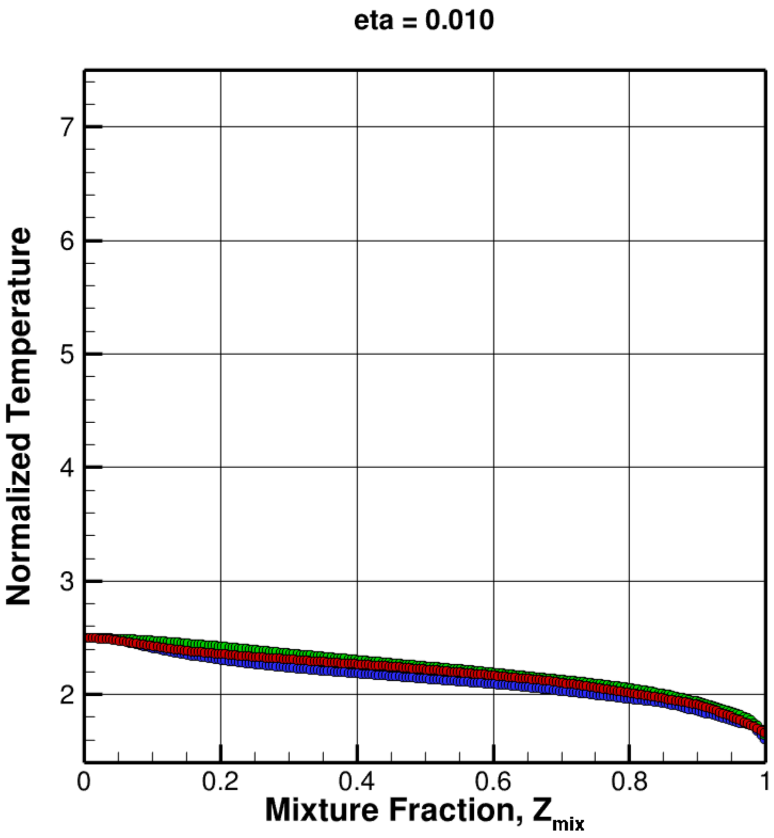
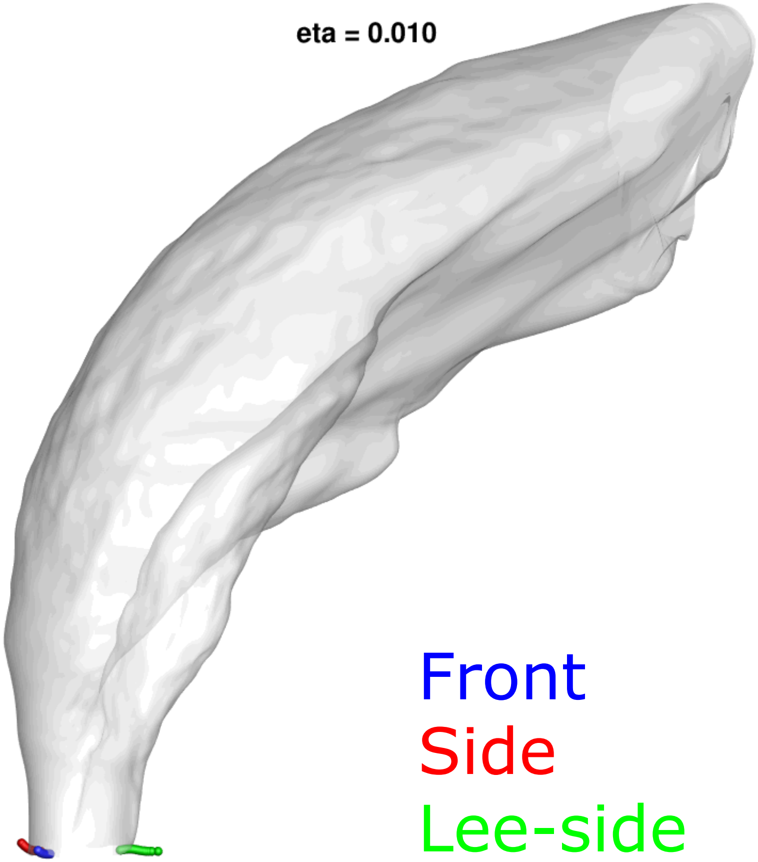
[1] Grout et al. Proc. Combust. Inst. 2011; Kolla et al. US Nat. Meeting 2011

LES Combustion Modeling

- Evolution of 1D-flamelet-elements in JICF

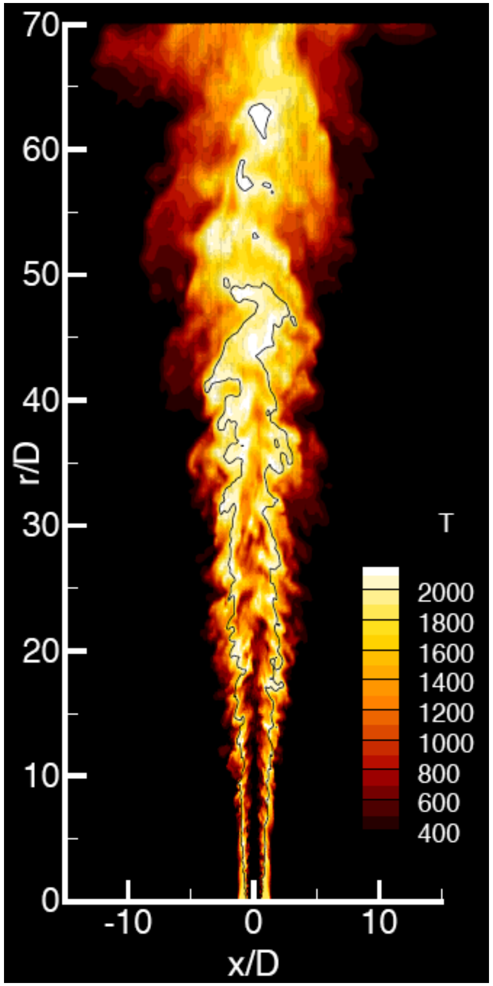




Front
Side
Lee-side

LES Combustion Modeling

- LES Flamelet-based combustion models
  - Parameterization of combustion process in terms of reduces set of scalars
  - Account for detailed chemistry
  - Tabulation of reaction chemistry
  - Consideration of turbulence chemistry coupling



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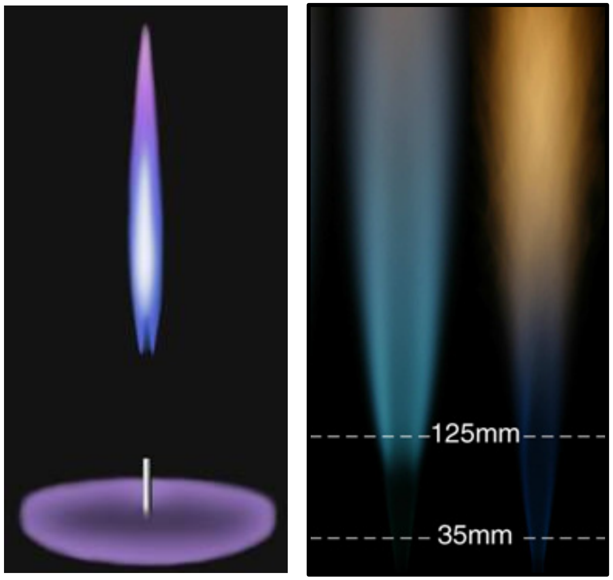
Autoignition in Turbulent Flames

- Modeling challenges in predicting autoignition in turbulent flames
  - Autoignition is transient process; requires accurate description of temporal flame-evolution
  - Flame stability and ignition dynamics strongly dependent on scalar mixing and flame/turbulence interaction



- Modeling approach[1]
  - Autoignition requires consideration of transient species formation,
    described by unsteady flamelet equations
  - Turbulence/chemistry interaction: Presumed PDF-closure to consider effects of subgrid-mixing and unresolved flame structure

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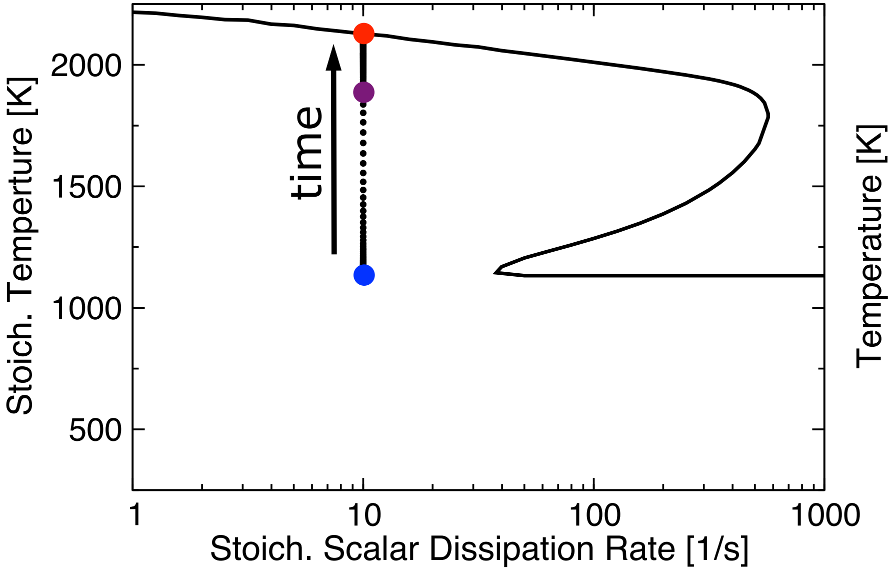
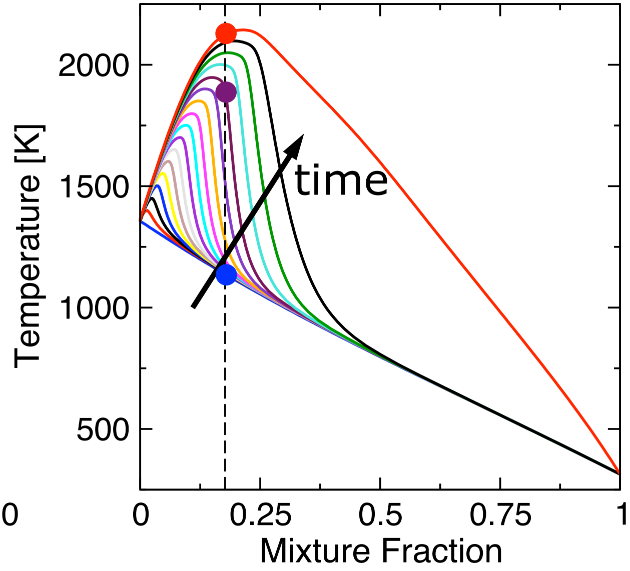
[1] Ihme & See, Combustion & Flame, 157, 2010

Autoignition in Turbulent Flames

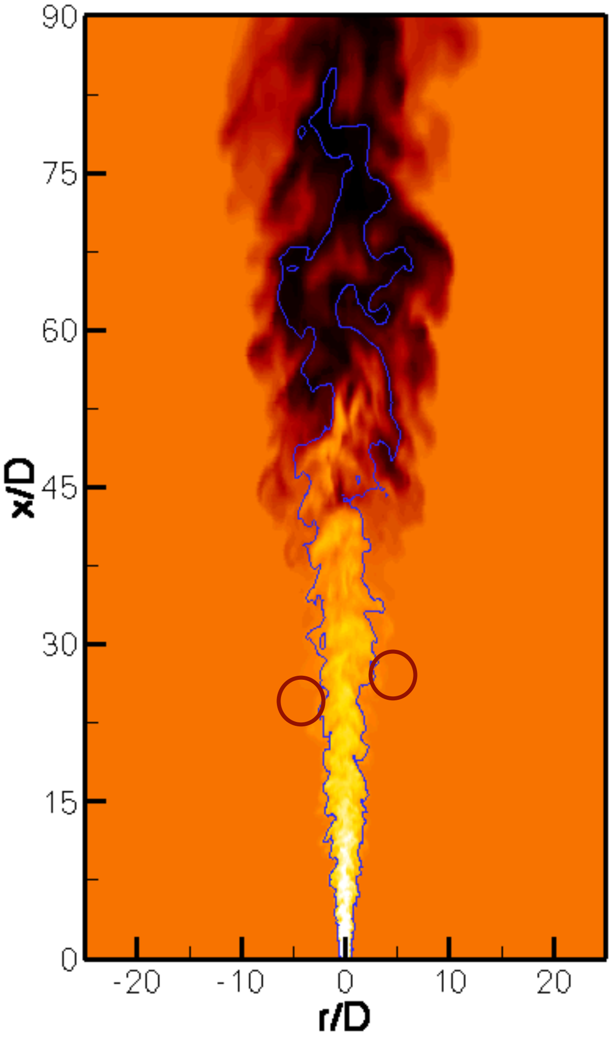
- Conditions for flame-ignition in diffusion flames
  - Autoignition is transient process
  - Sufficiently low scalar dissipation rate
  - Flame ignition occurs under conditions corresponding to "most-reactive mixture"
  - Build-up of radical pool through chain-branching reaction





Autoignition in Turbulent Flames

- Experimental configuration
  - Lifted flame in vitiated co-flow
  - Fuel: methane/air 1:2
  - Co-flow temperature: 1350 K
  - Co-flow composition from premixed H_2-Air reaction product
- Computational setup
  - Grid: 2.5 Mio grid points
  - Reaction Chem.: GRI 2.11, (also used GRI 3.0, USC-mech II)
  - 5-dimensional chemistry table with grid-refinement



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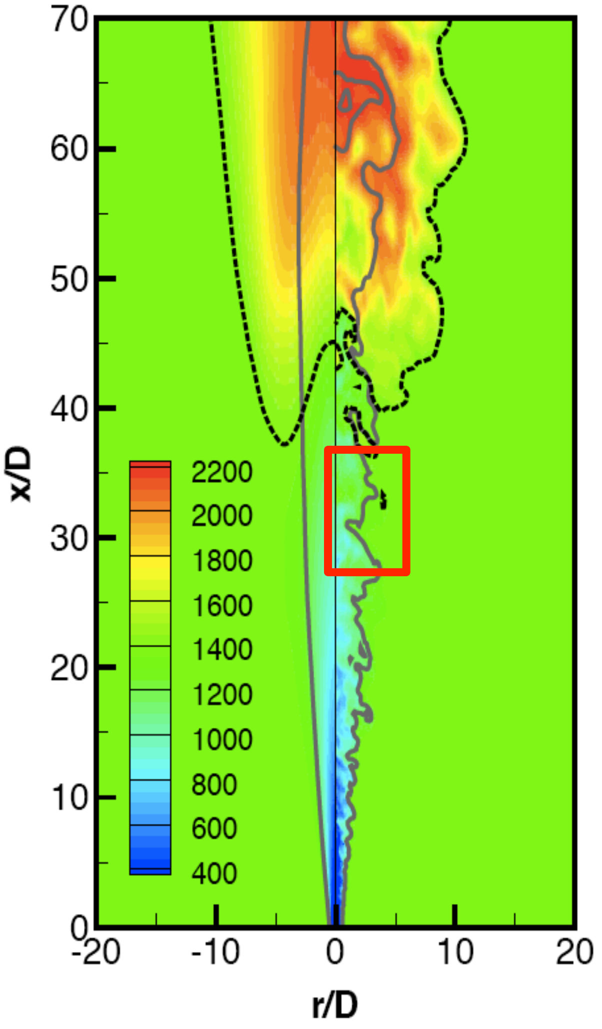
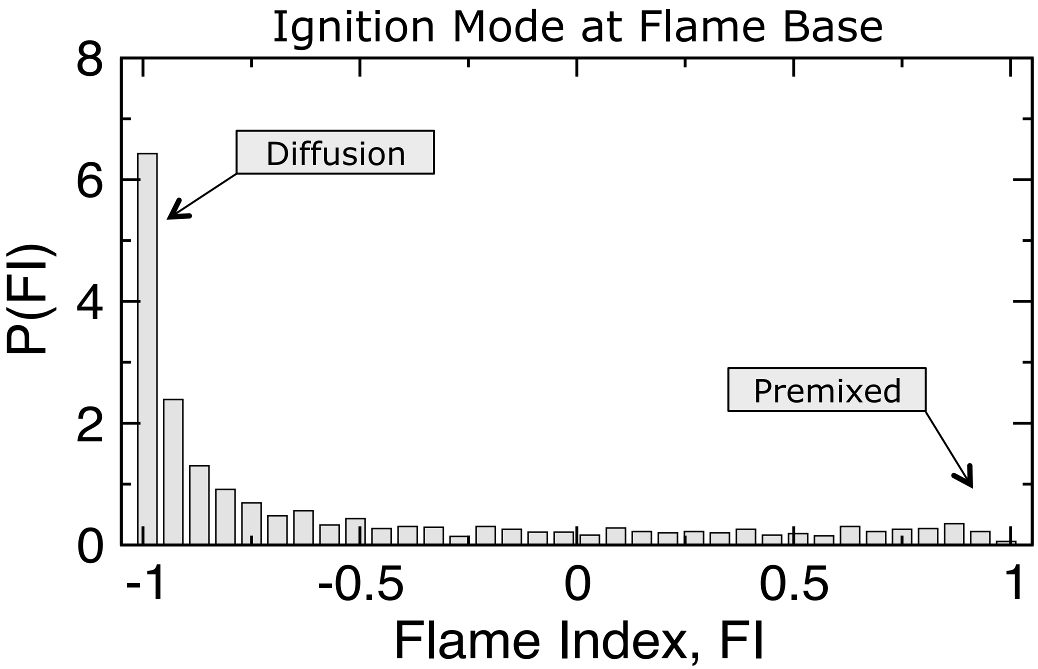
[1] Cabra, Chen, Dibble, Karpetis, Barlow, CF, 143, 2005

Autoignition in Turbulent Flames

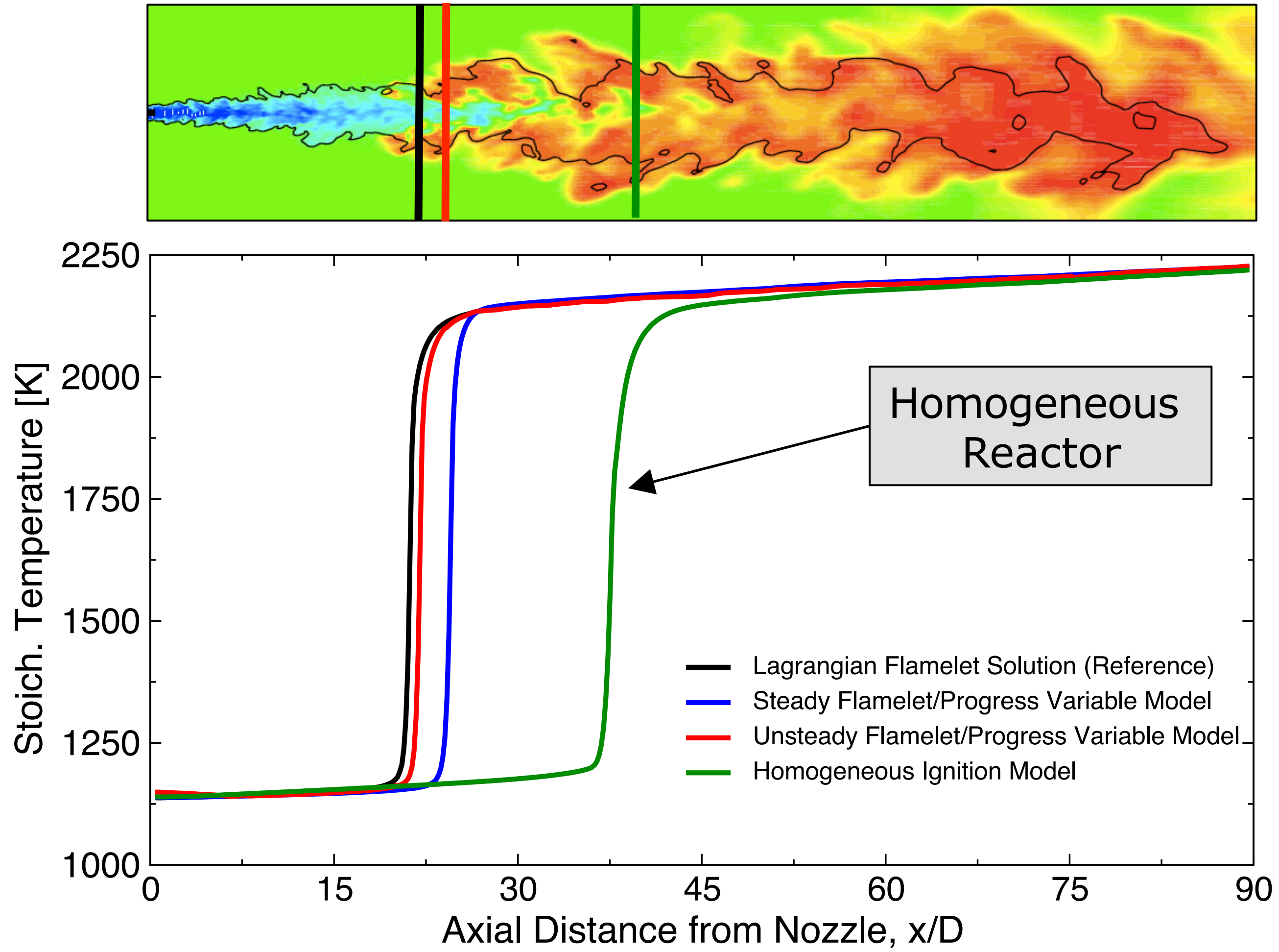




- Ignition conditions: low-strain region at most-reactive mixture composition
- Ignition occurs primarily in diffusion regime
- Location of flame-base controlled by HO_2-radical pool that is formed upstream of flame

Autoignition in Turbulent Flames

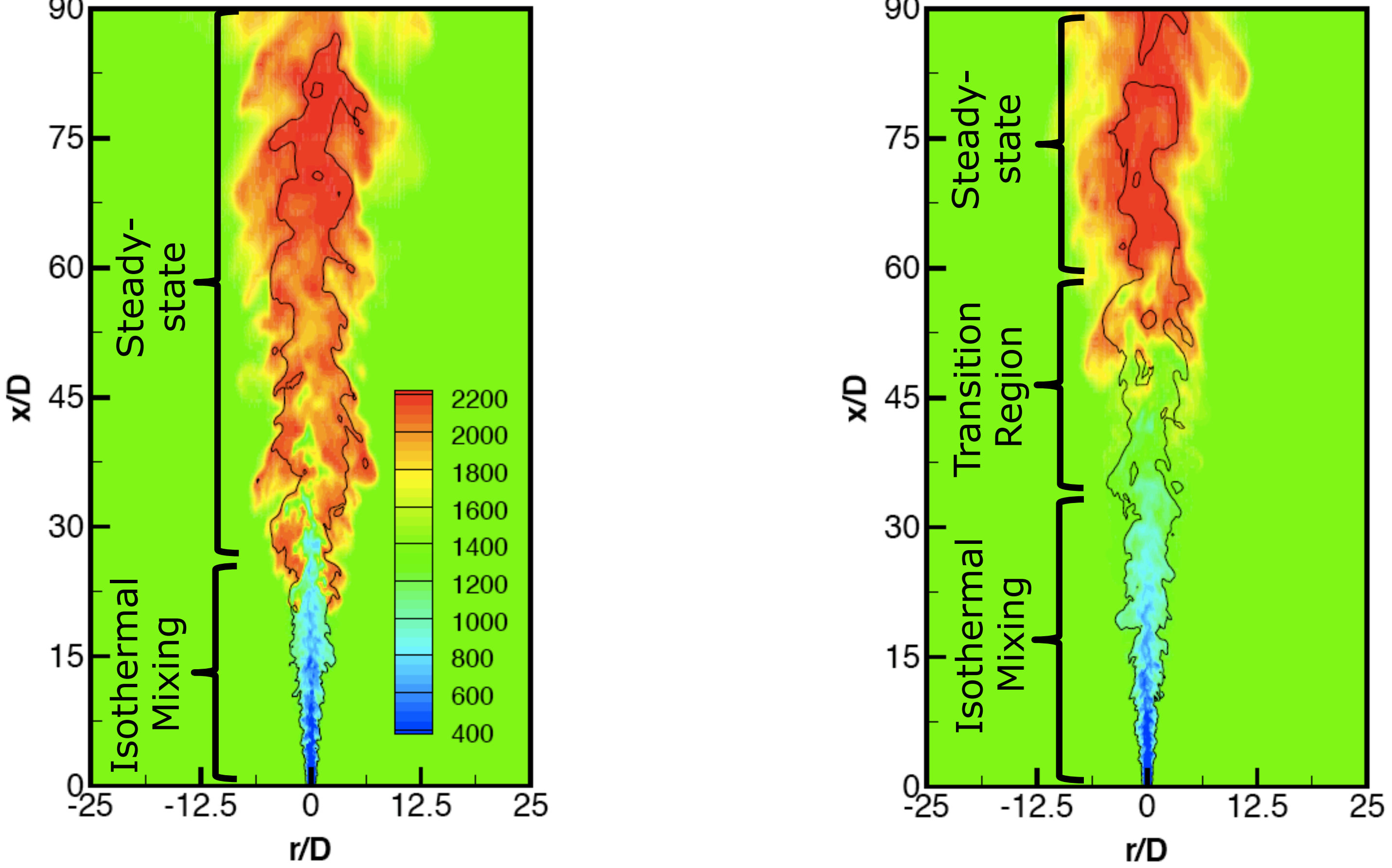
- Effects of turbulence and scalar mixing



Homogeneous Reactor

Autoignition in Turbulent Flames

- Instantaneous temperature field

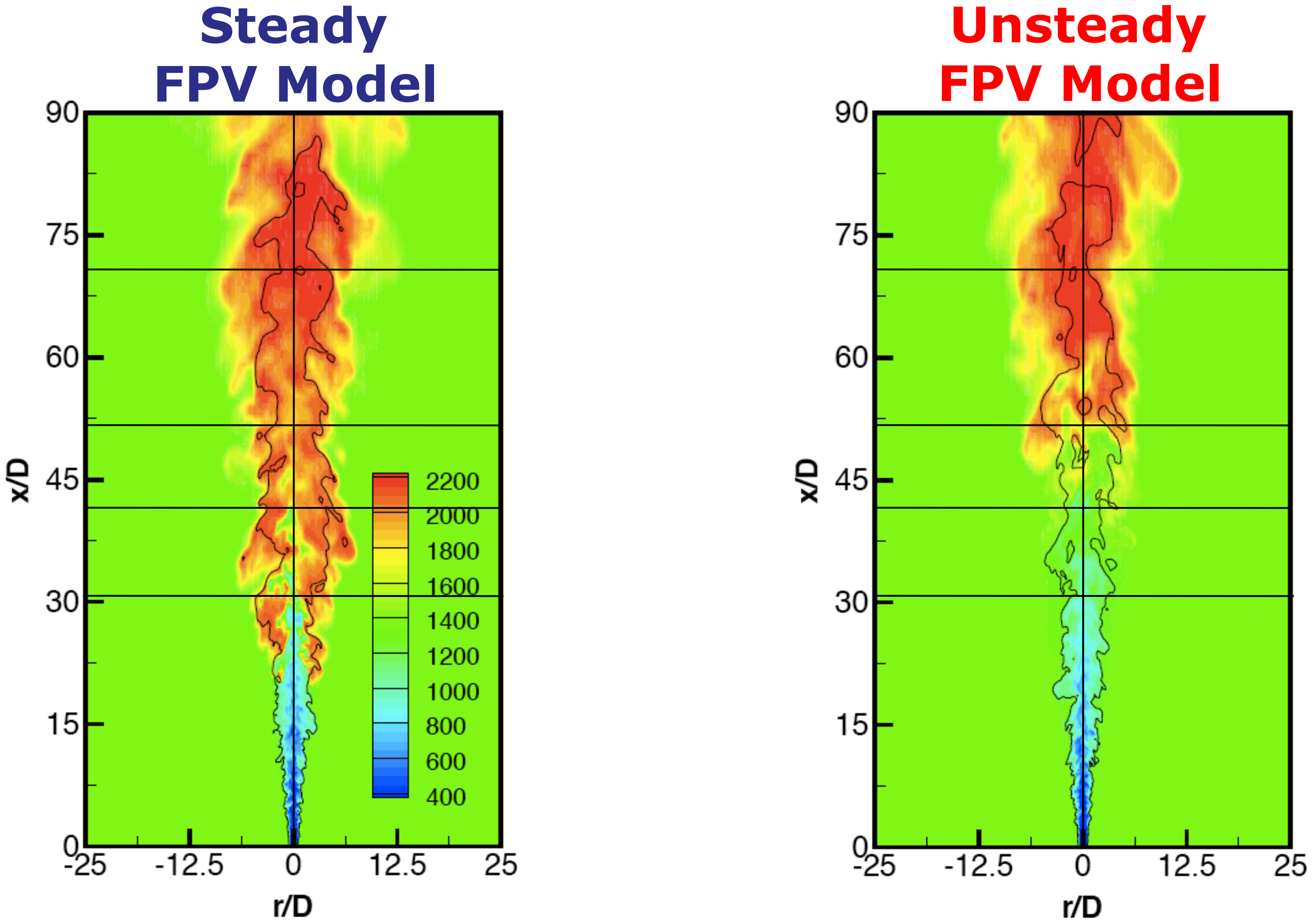


Steady FPV Model

Unsteady FPV Model

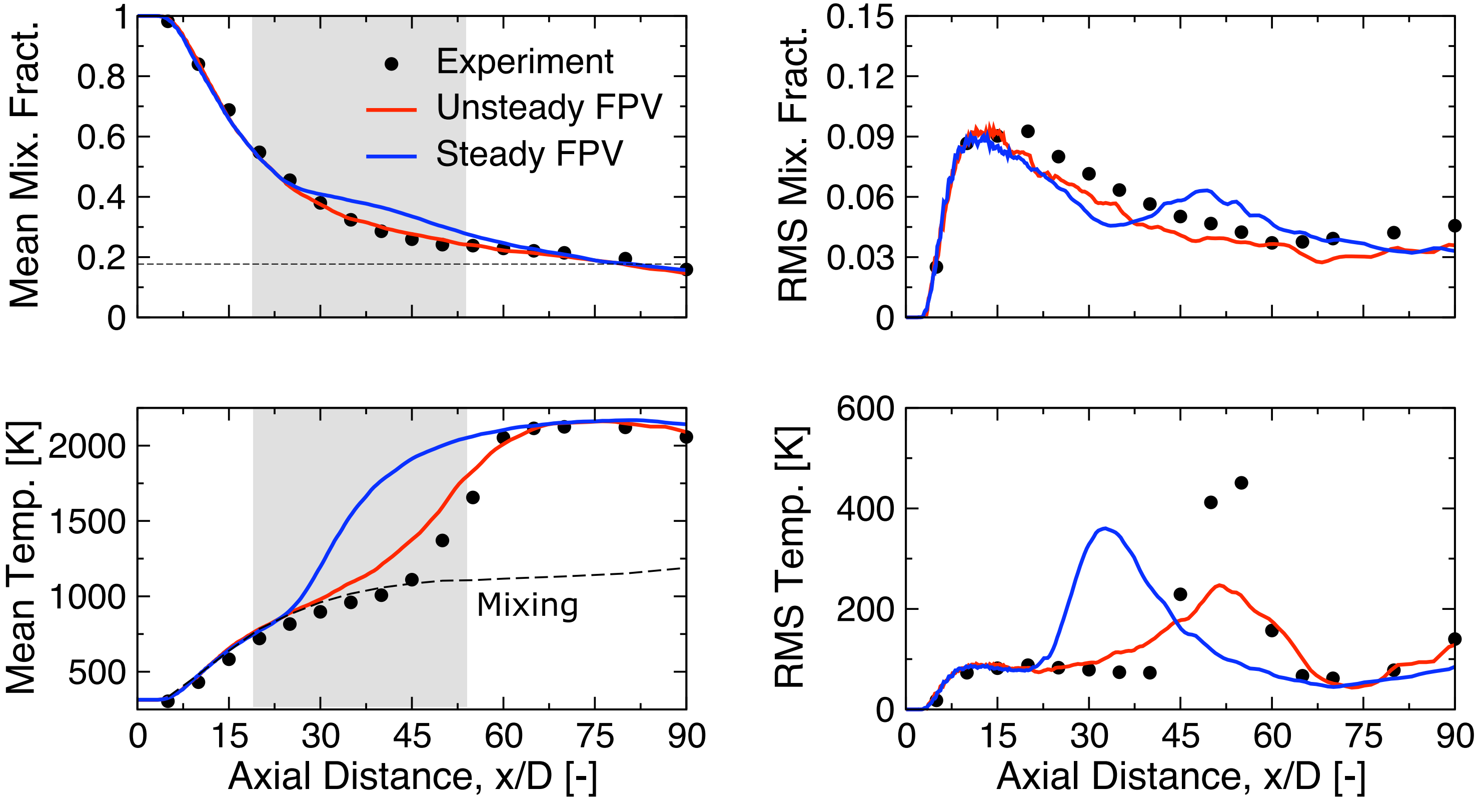
Autoignition in Turbulent Flames

- Instantaneous temperature field



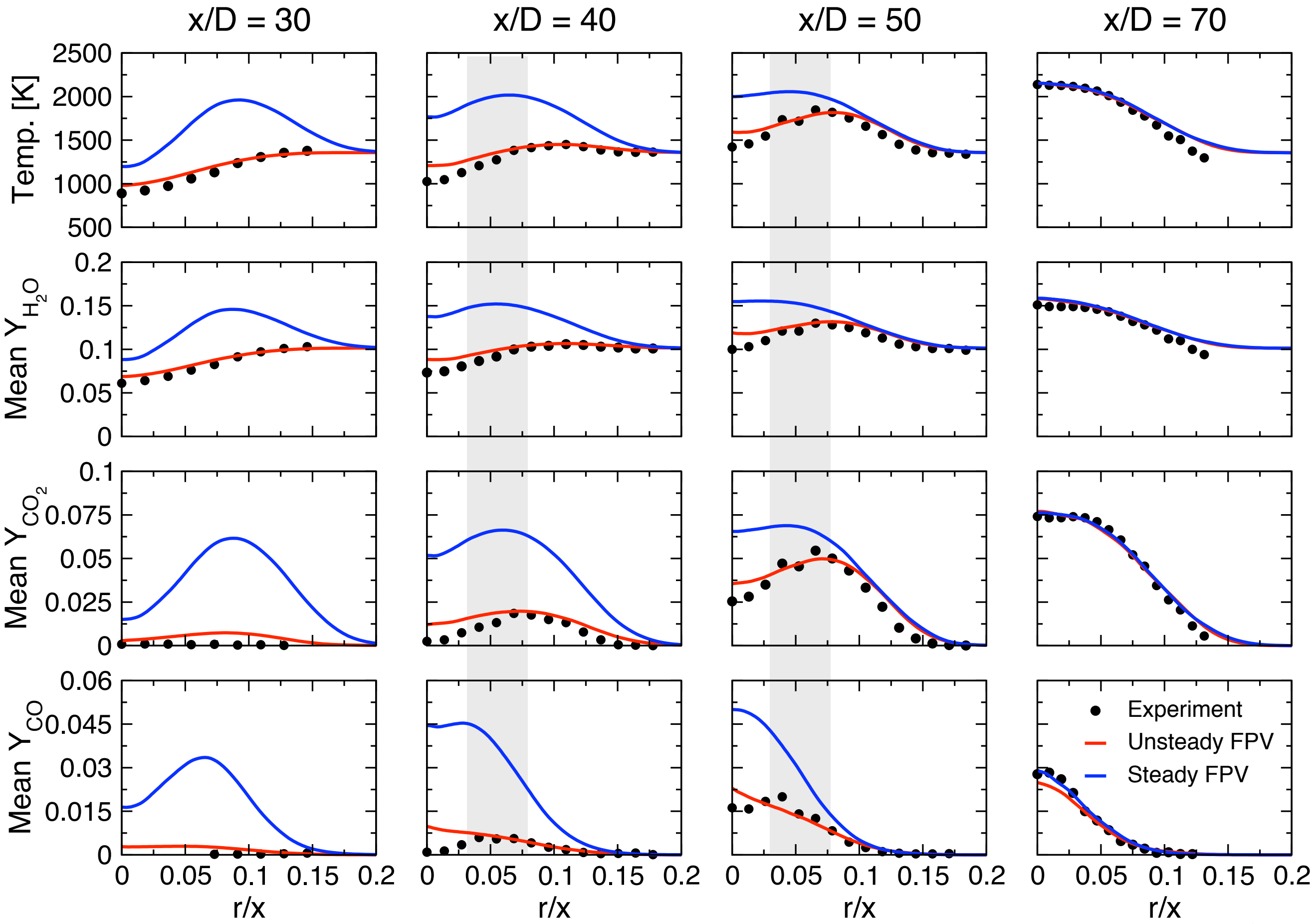
Autoignition in Turbulent Flames

- Centerline profiles



Autoignition in Turbulent Flames

- Radial profiles



Nozzle down-stream direction

Summary and Conclusions

- LES-modeling of lifted vitiated flames

- Key modeling components
  - Transient flame evolution
  - Accurate description of turbulent mixing and scalar dissipation rate

- Combustion-physical insights
  - Transient flame evolution
  - Identified significance of flame/turbulence interaction

→ Homogeneous reactor-model under-predicts ignition onset

Overview

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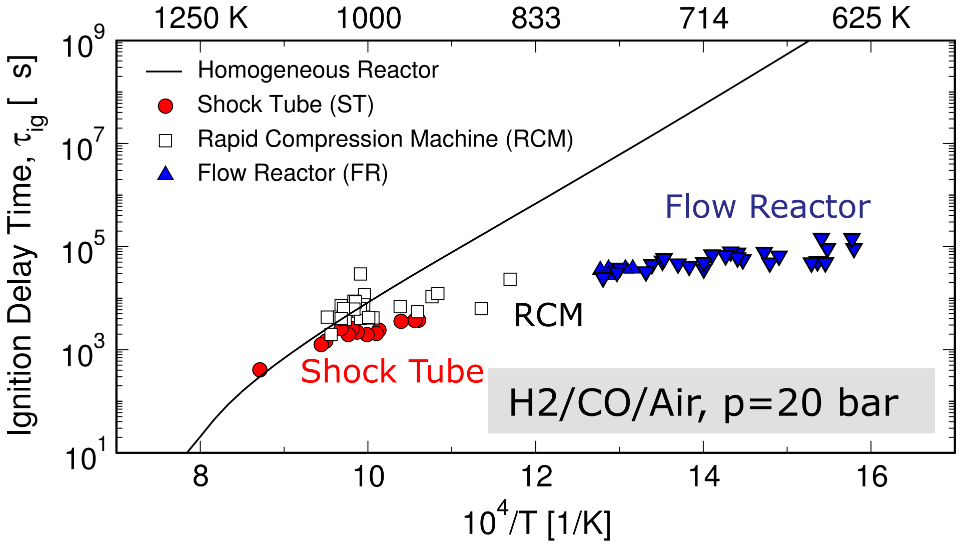
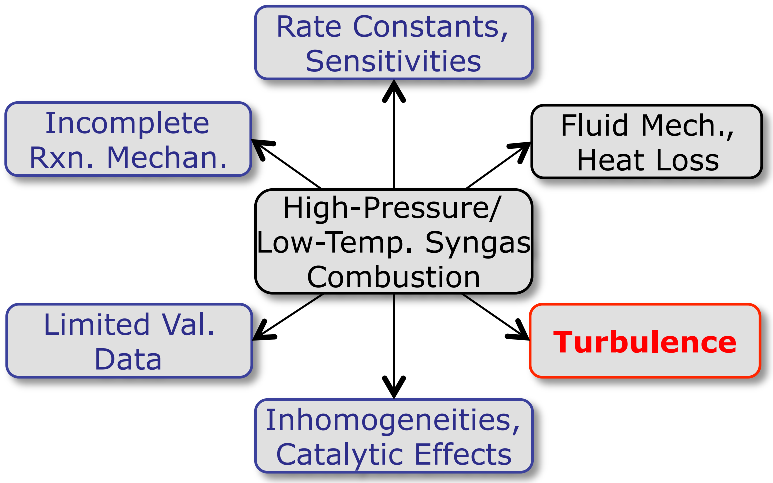
Turbulent Inhomogeneities and Facility Effects

- Question: Can we apply “lessons-learned” from LES simulations to characterize experimental facilities?
  - Shock-tubes
  - Flow-reactors
  - Rapid compression machines

- Source of non-idealities in experimental facilities[1,2,3]





High-Pressure/ Low-Temp. Syngas Combustion

Rate Constants, Sensitivities

Incomplete Rxn. Mechan.

Fluid Mech., Heat Loss

Limited Val. Data

Turbulence

Inhomogeneities, Catalytic Effects

---

1 Petersen et al., Comb. & Flame, 149, 244 (2007); 2 Chaos & Dryer, Combust. Sci. and Tech., 180, 1053 (2008); 3 Burke, Chaos, Dryer, & Ju, Comb. & Flame, 157, 618 (2010)

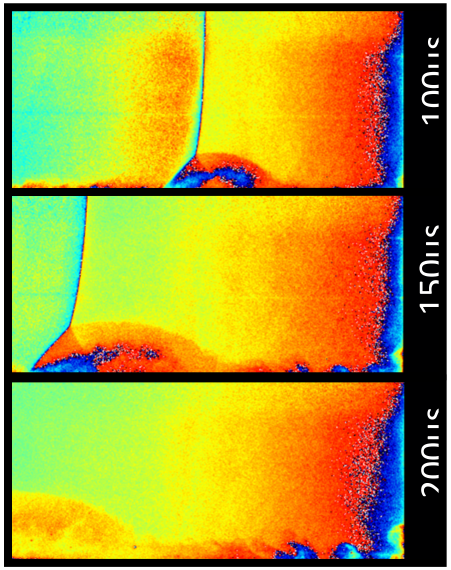
Turbulent Inhomogeneities and Facility Effects

- Research Objectives
  - Use high-fidelity simulation and non-equilibrium formulation to isolate parametric contributions of non-idealities in experimental facilities
  - Research emphasis
    - Identify parametric sensitivities
    - Reconcile observed differences between experiments and detailed model-formulations
  - Facilities
    - Shock-tube
    - Flow-reactor
    - Rapid compression machine

Turbulent Inhomogeneities and Facility Effects

Shock-Tube

- Non-ideal processes in shock-tubes

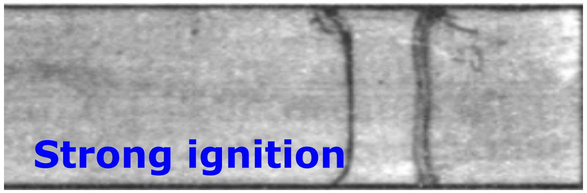


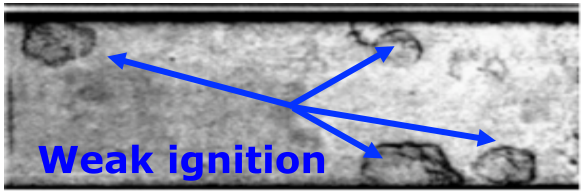
1. Non-ideal rapture of diaphragm[#]
- Finite opening time of diaphragm
- Contribution to shock attenuation: 30%

2. Boundary layer growth[$]
- Formation of viscous boundary layer behind initial shock

3. Shock reflection and bifurcation[%]
- Lift-off of boundary layer resulting in formation of separation region

4. Inhomogeneous ignition and weak-to-strong ignition transition[$]
- Ignition proceeds as multi-dimensional heterogeneous process





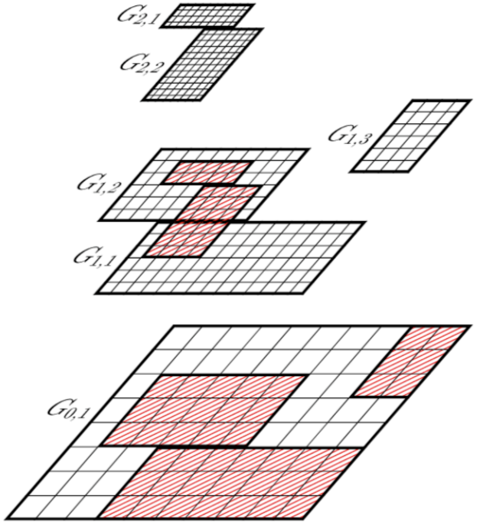
[#] Petersen, E. L. & Hanson, R., Shock Waves, 10 (2001); [$] Mirels, H., NACA-TN 3278 (1956); Mirels, H., NACA-TN 3401 (1955); [%] Yoo, Mitchell, Davidson, Hanson, Shock Waves, 21, 2011

Turbulent Inhomogeneities and Facility Effects

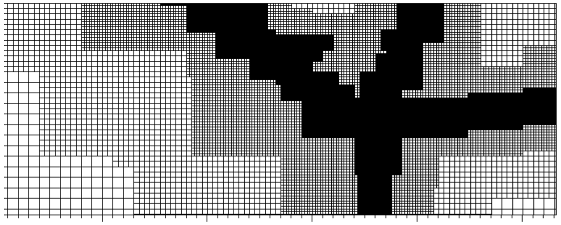
Shock-Tube

- Modeling challenges in simulating shock-tubes
  - Disparity of spatial and temporal scales

$$\underbrace{\frac{1}{150\,\mathrm{Re}_\tau^{2/7}}}_{\text{Geometric shock-tube domain}} L \sim \frac{1}{\mathrm{Re}_\tau}\delta \sim \delta_v \sim \underbrace{\frac{\mathrm{Re}_\tau\,\mathrm{M}}{\mathrm{M_t}}}_{\text{Shock Thickness}}\xi$$



- Solution method: Adaptive mesh refinement
  - AMR exploits multiscale nature of hydro-dynamic problem by locally adjusting computational effort to maintain uniform level of accuracy#,$

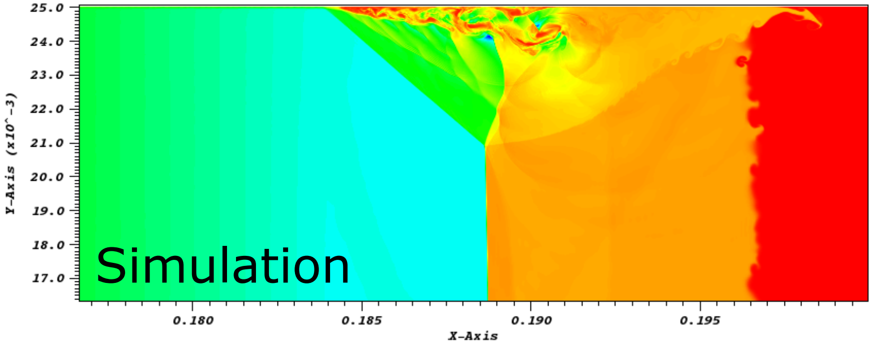


# Deiterding, R., Computers & Structures, 87, 769, 2009; $ Berger, M. & Colella, P., JPC, 1982 (1988); % C. Pantano, et al. JCP, 221 (1) (2006) 63–87.

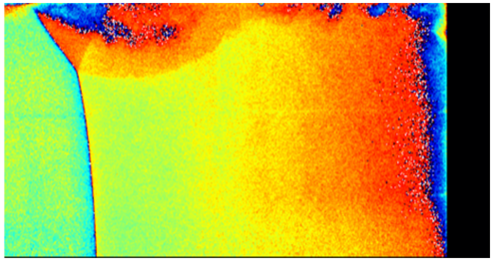
Turbulent Inhomogeneities and Facility Effects

Shock-Tube

- Shock-bifurcation
  - Simulation of Ar-diluted H_2/O_2 mixture at 5 and 10 bar pressure
    - →Relevant condition for weak and strong ignition regime
    - →Adiabatic and isothermal wall conditions
  - Shock tube setup
    - Length: 1m
    - Diameter: 5 cm
    - Helium in driver section
  - Target condition:
    - T_5=1100 K, p_5=10 bar
  - Chemical mechanism:
    - Burke et al.[1] (2011)



Experiment[2]



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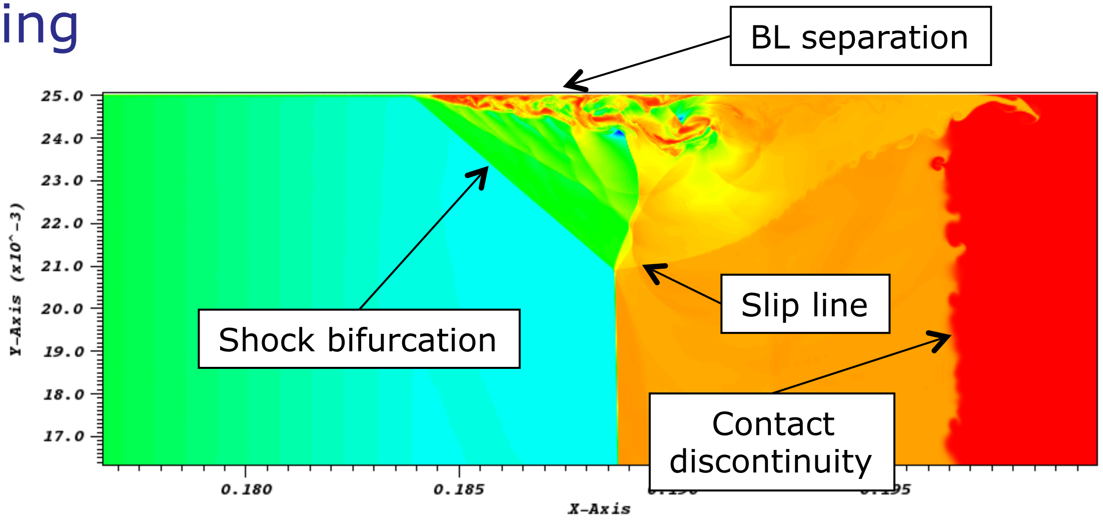
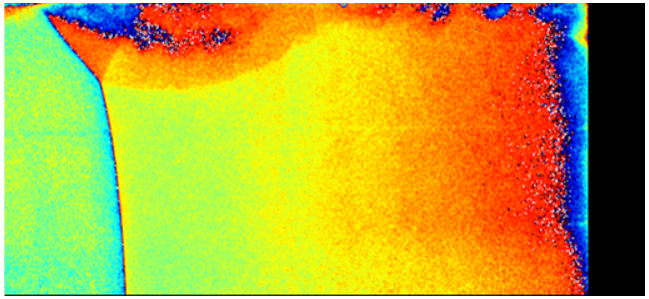
1 Burke, Chaos, Ju, Dryer, Klippenstein, IJCK, 44, 2011

2 Yoo, Mitchell, Davidson, Hanson, Shock Waves, 21, 2011

Results: Shock Bifurcation

- Shock-bifurcation
  - Instantaneous temperature evolution shows rich flow-field structure: Boundary layer separation, Shock-bifurcation, Boundary heating





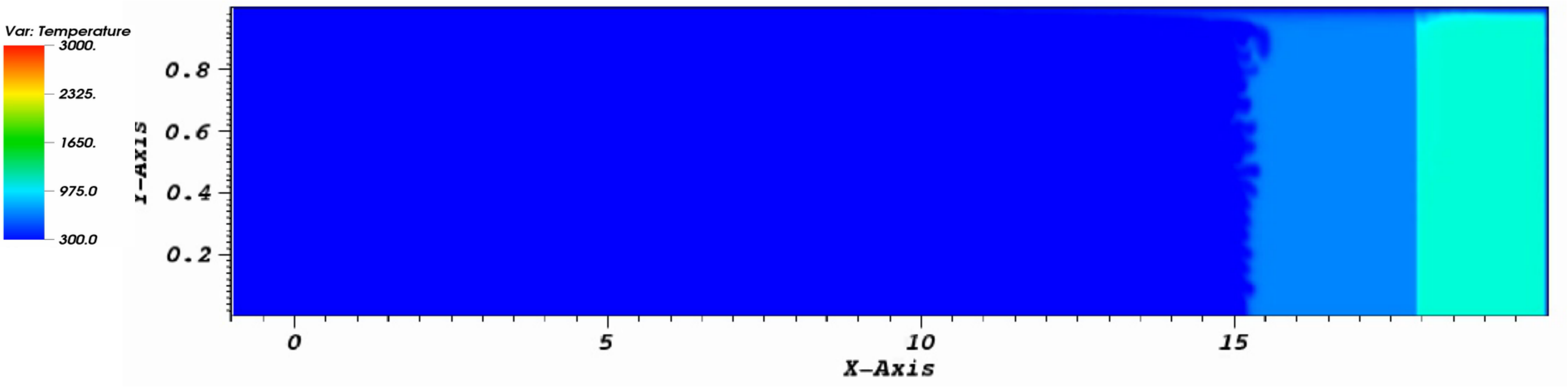
Toluene PLIF Measurements[#]

[#] Yoo, Mitchell, Davidson, Hanson, Shock Waves, 21, 2011

Turbulent Inhomogeneities and Facility Effects

Shock-Tube

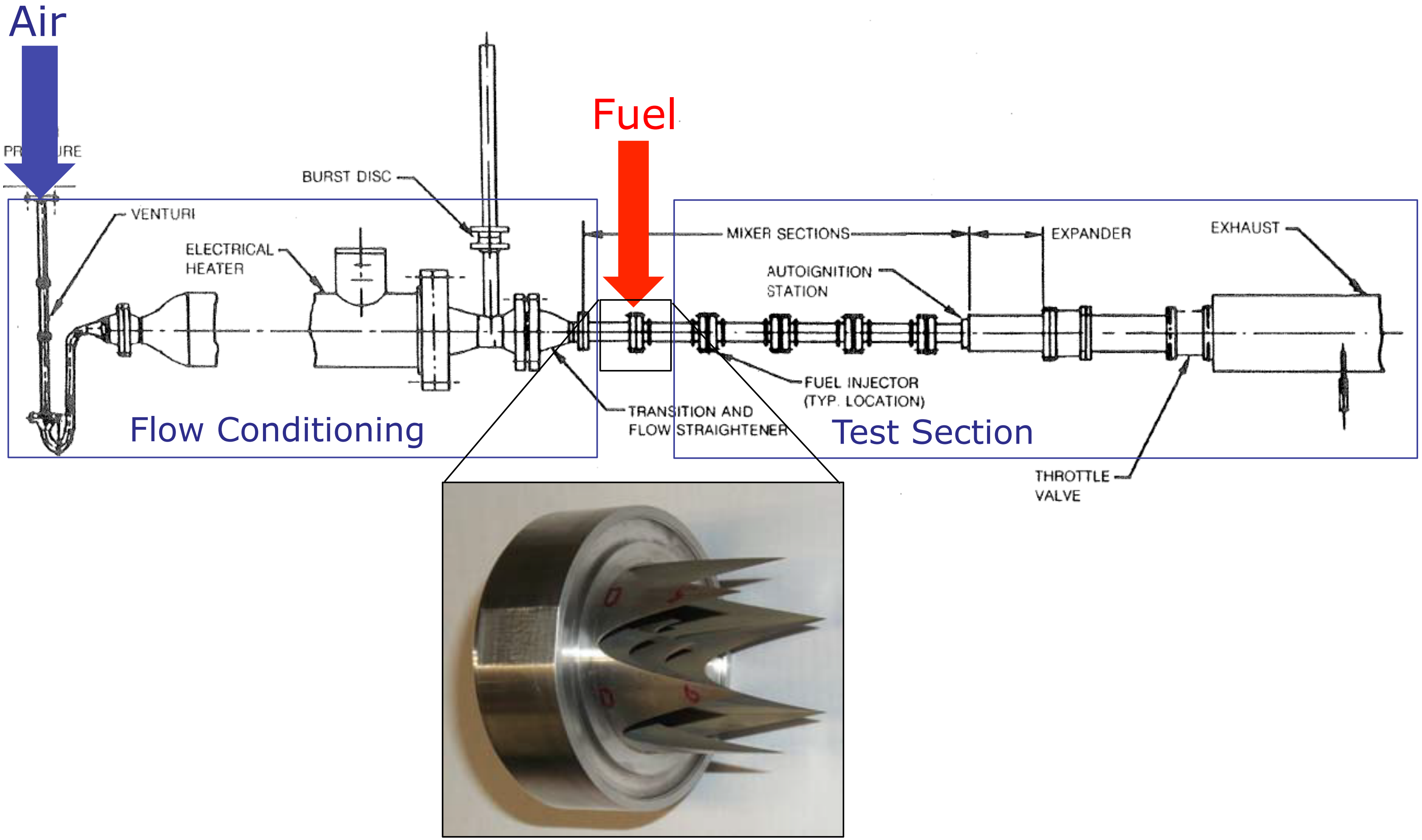
- Ignition
  - Isothermal wall



  - Observations:
    - Ignition is initiated at end-wall
    - Flame propagation towards unburned mixture (region of favorable pressure gradient)
      → non-homogeneous ignition

Turbulent Inhomogeneities and Facility Effects

Flow-Reactors



Air

Fuel

Flow Conditioning

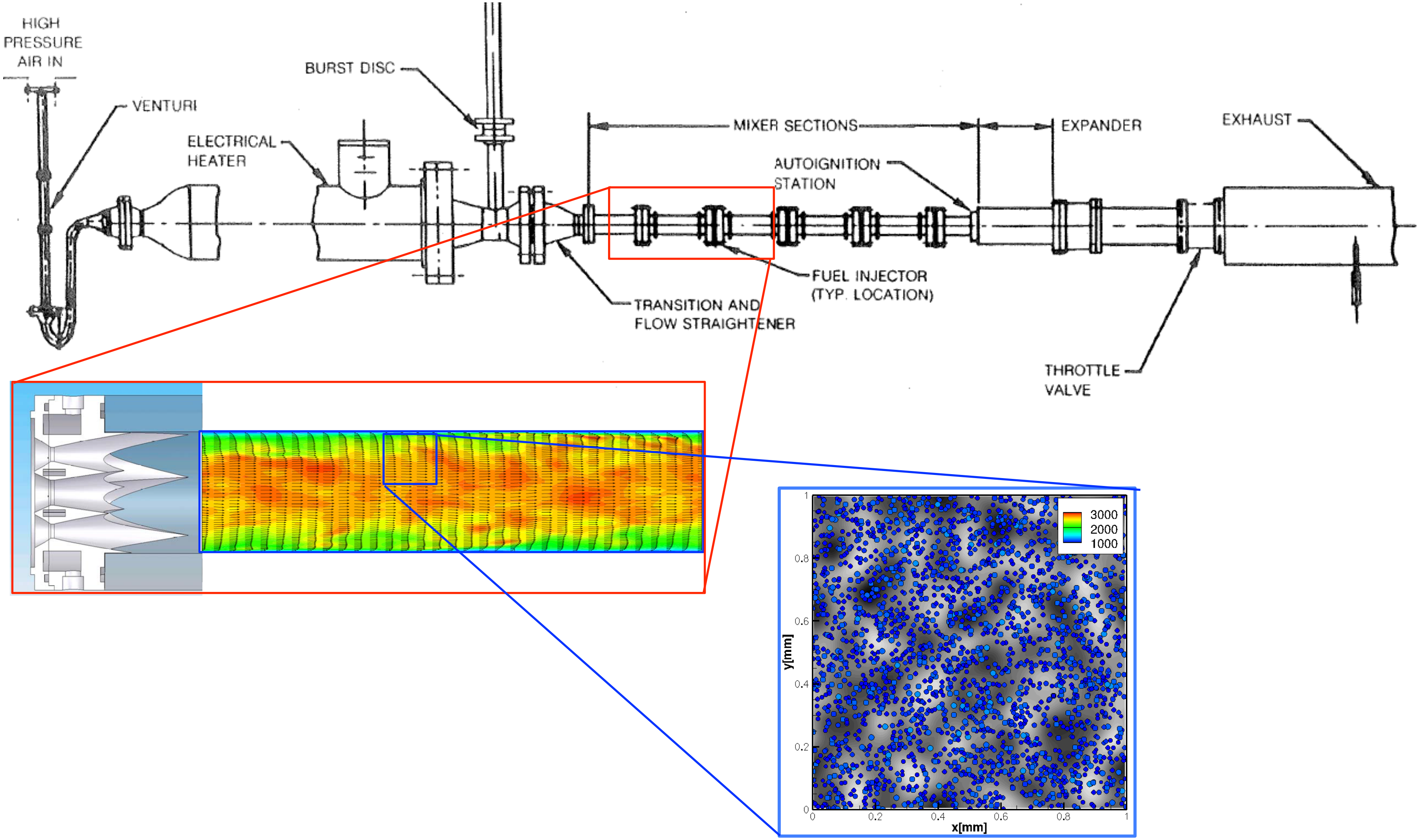
Test Section

BURST DISC
VENTURI
ELECTRICAL HEATER
MIXER SECTIONS
EXPANDER
EXHAUST
AUTOIGNITION STATION
FUEL INJECTOR (TYP. LOCATION)
TRANSITION AND FLOW STRAIGHTENER
THROTTLE VALVE

Peschke & Spadaccini, (1985); Santoro (2009)

Turbulent Inhomogeneities and Facility Effects

Flow-Reactors

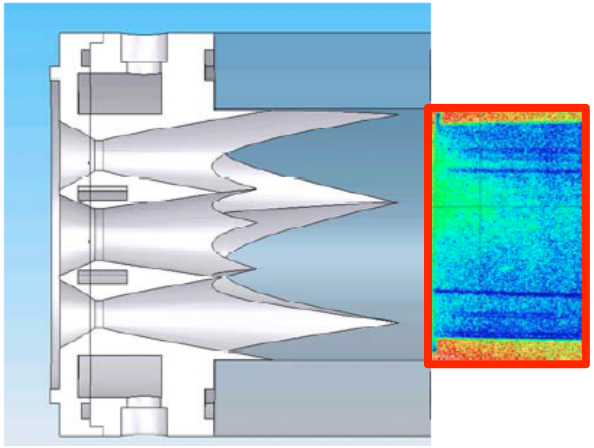

HIGH PRESSURE AIR IN
VENTURI
ELECTRICAL HEATER
BURST DISC
MIXER SECTIONS
EXPANDER
EXHAUST
AUTOIGNITION STATION
FUEL INJECTOR (TYP. LOCATION)
TRANSITION AND FLOW STRAIGHTENER
THROTTLE VALVE
3000
2000
1000
y[mm]
x[mm]
0
0.2
0.4
0.6
0.8
1

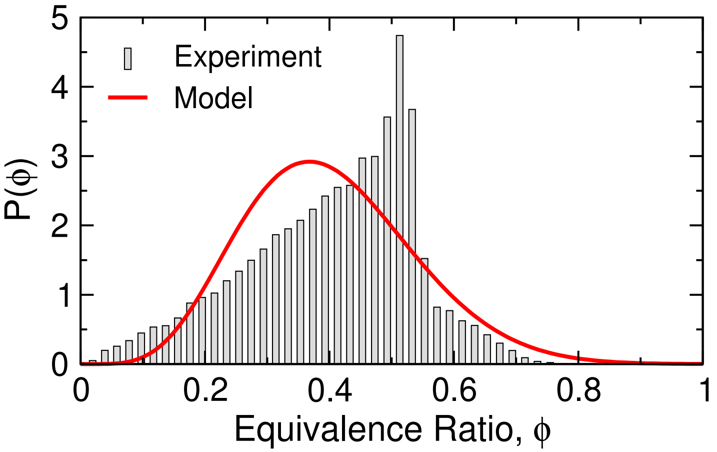
Peschke & Spadaccini, (1985); Santoro (2009)

Turbulent Inhomogeneities and Facility Effects

Flow-Reactors

- Experimentally observed stochastic ignition suggests sensitivity to initial conditions
  - Mixture composition
  - Temperature
    - Unsteady heating
    - Wall-heat losses
    - Temp-difference btw. fuel and oxidizer
- Consider inhomogeneities
  - Equivalence ratio: sample from experimentally determined beta-distribution
  - Temperature fluctuations: Sample from Gaussian with specified *T′*
- Use fully-developed turbulent pipe-flow at Re = 10^4





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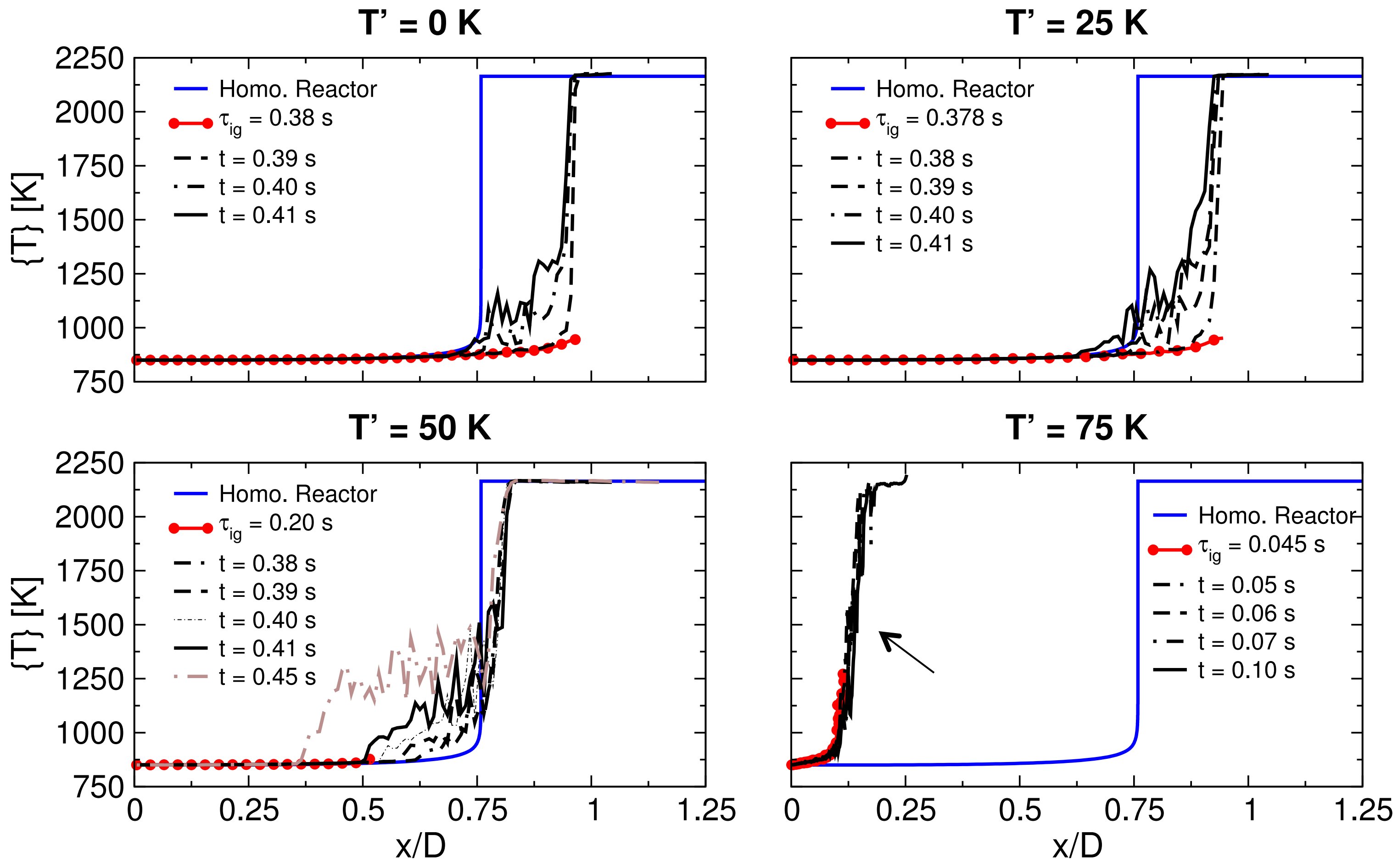
1 Santoro (2009)
2 Samuelsen et al. (2003)

Turbulent Inhomogeneities and Facility Effects

Flow-Reactors

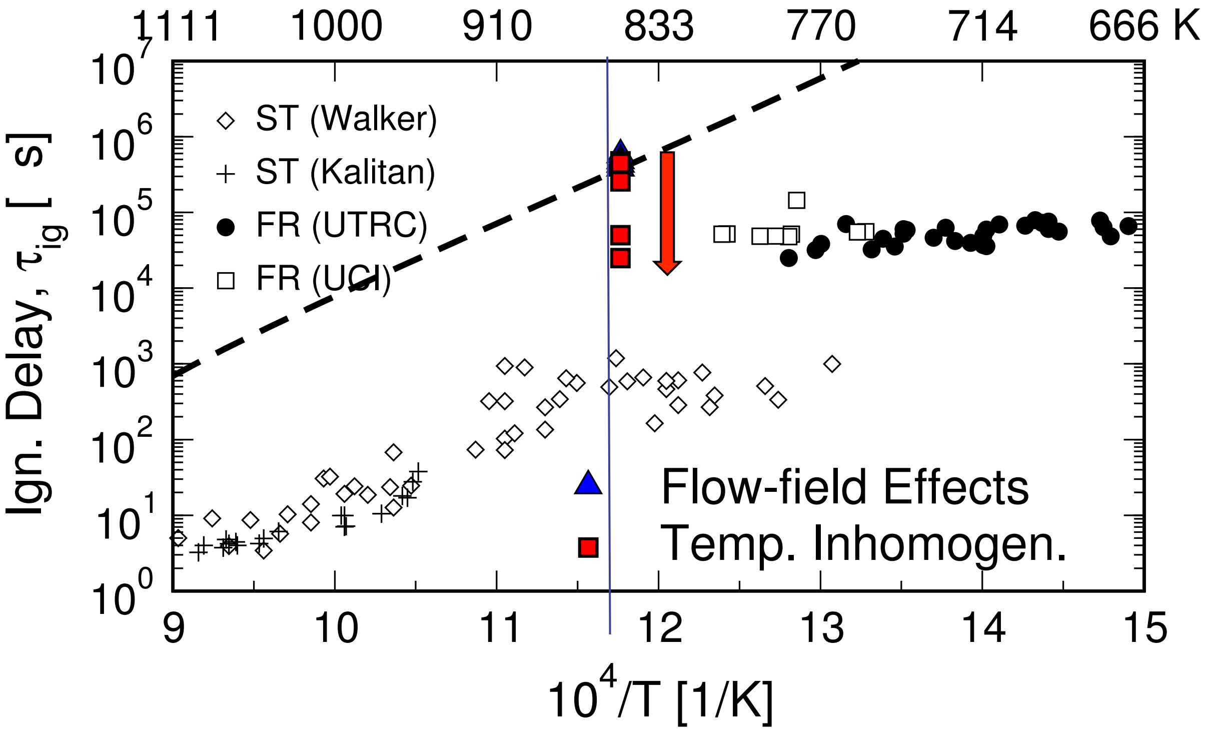
- Mixture variation: $\phi=0.4$; $\phi'=0.135$
- Temperature variation: T=850 K; T′ = {0, 25, 50, 75} K



Turbulent Inhomogeneities and Facility Effects

Flow-Reactors

- Mixture variation: ϕ=0.4; ϕ'=0.135
- Temperature variation: T=850 K; T' = {0, 25, 50, 75} K



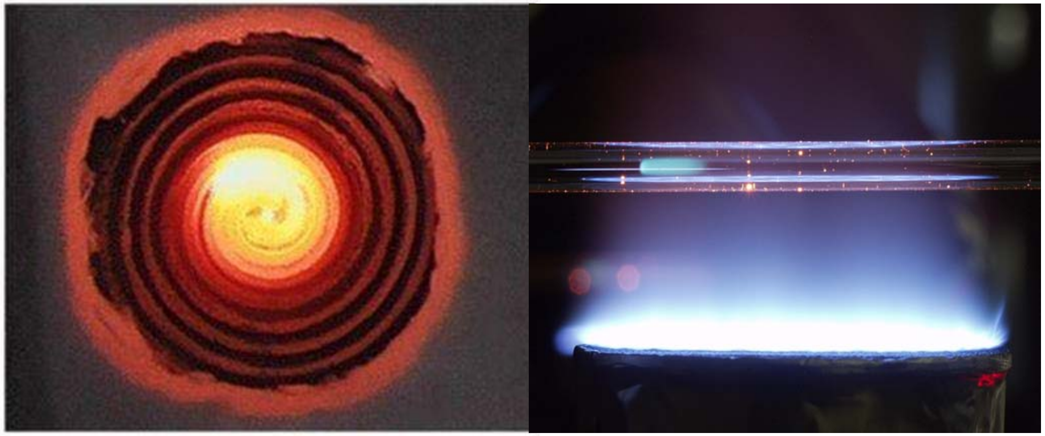
Summary and Conclusions

- Turbulence/chemistry coupling processes
  - Increased relevance for low-Damkoehler/high-Karlovitz combustion processes: oxygen-diluted comb.; autoignition; preheat-comb.
  - Turbulence promotes mixing, exchange of radicals and enthalpy
  - Ignition occurs at preferred sites: “most-reactive” mixture and regions of low strain

- Validated high-fidelity LES combustion models have been developed and are available to accurately capture ignition processes
  - Models rely on experimental data

- Simulations can assist and complement experimental investigations
  - Identify experimental sensitivities
  - Guide potential modifications to mitigate facility effects
  - Reconcile discrepancies btw. experiments and theory
  - Example: Turbulence/chemistry coupling in shock-tubes and flow-reactors

The First International Workshop on Flame Chemistry, July 28 - 29, 2012, Warsaw, Poland



Micro flow reactor with prescribed temperature profile

Toward fuel Indexing and kinetics study based on multiple weak flames

Kaoru Maruta, Tohoku Univ.

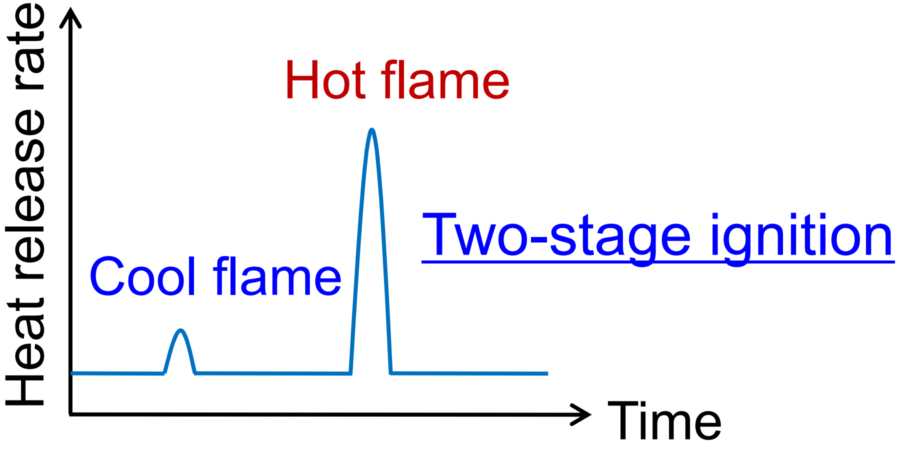
S. Minaev, N.I. Kim, T. Yokomori, H. Nakamura, S. Hasegawa, T. Tezuka
T. Kataoka, Y. Tsuboi, H. Oshibe, A. Yamamoto, R. Tanimoto, M. Hori,
K. Saruwatari, S. Suzuki, T. Kamada, X. Li, Y. Kizaki, T. Onishi and H. Takahashi

Background and objectives

For understandings ignition and combustion characteristics of practical fuels…

Data from
Shock tube and RCM
have been extensively used

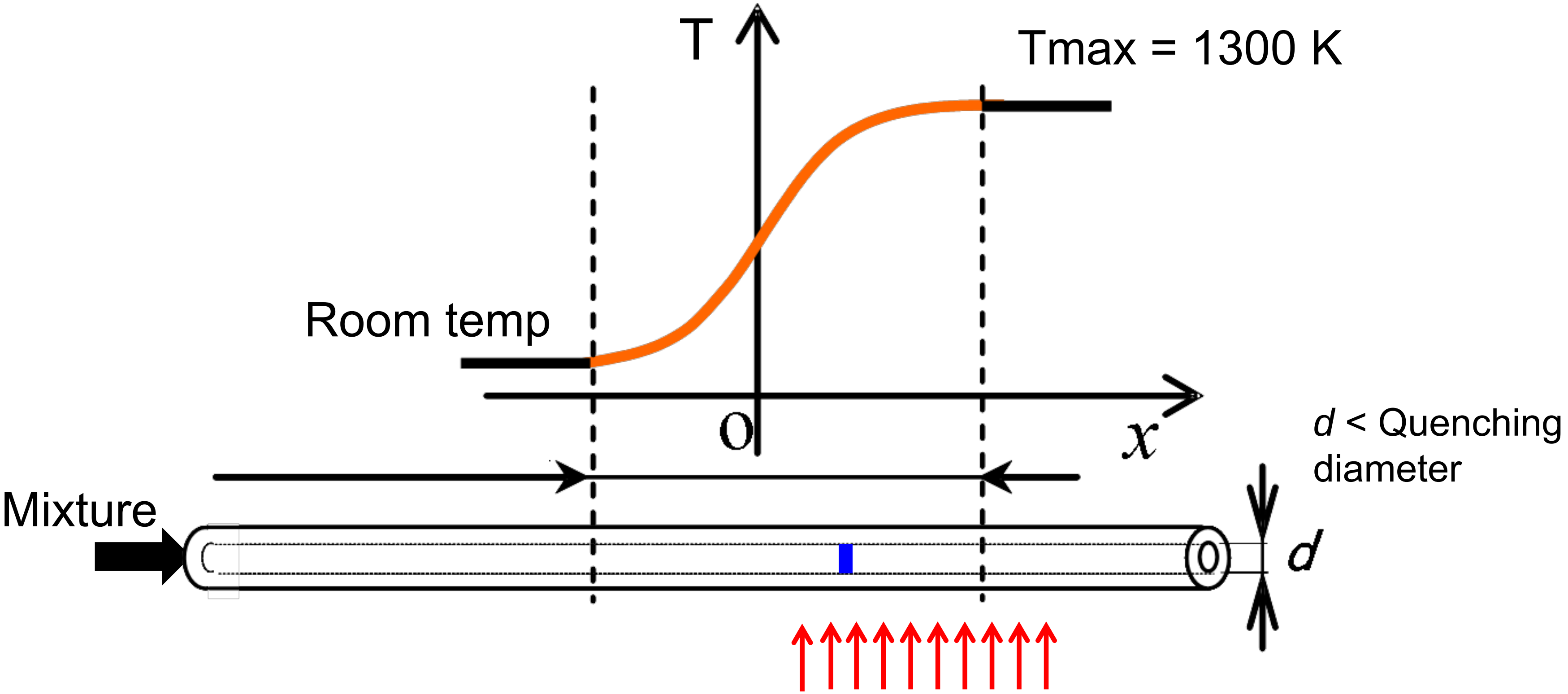
Ignition delay


Heat release rate
Hot flame
Two-stage ignition
Cool flame
Time

Micro flow reactor with prescribed temperature profile

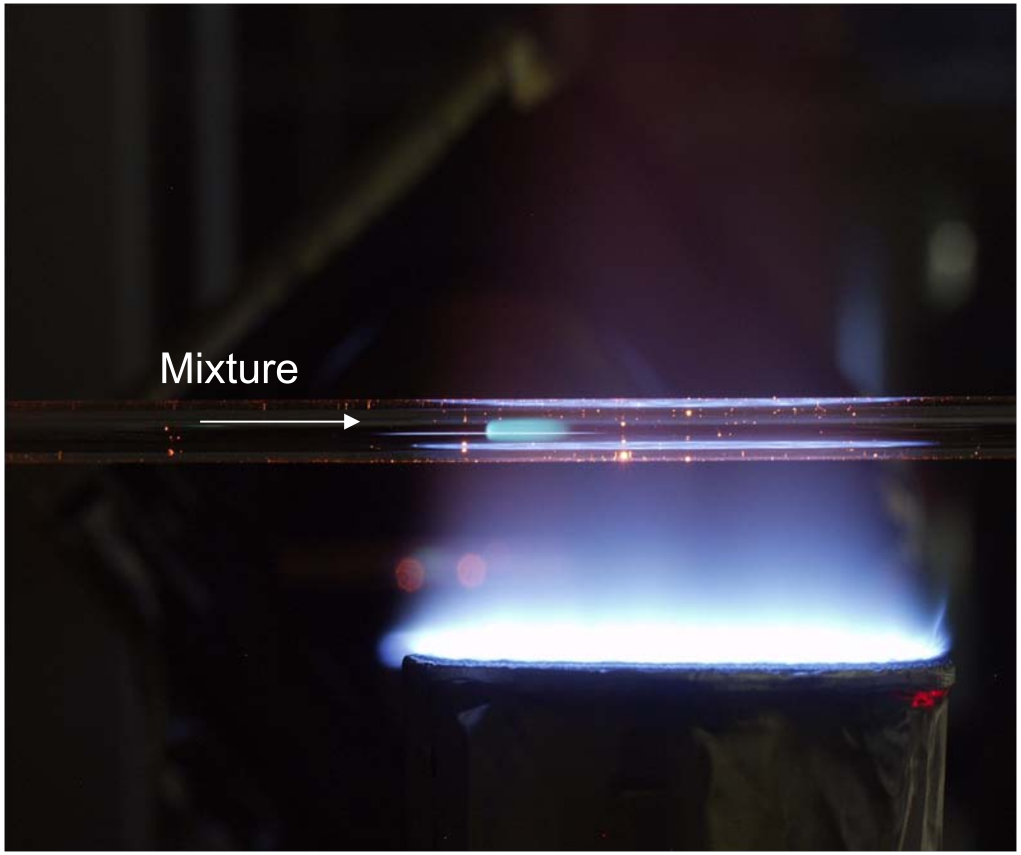
Single or multiple weak flames

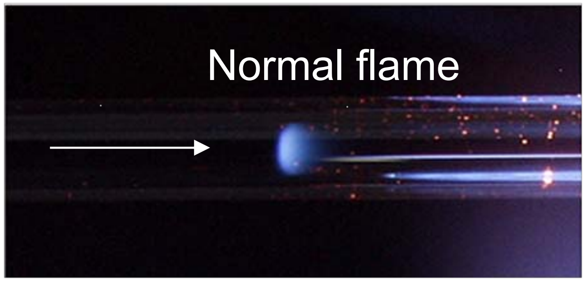
Micro flow reactor with prescribed temperature profile


T
Tmax = 1300 K
Room temp
O
x
d < Quenching diameter
Mixture
d

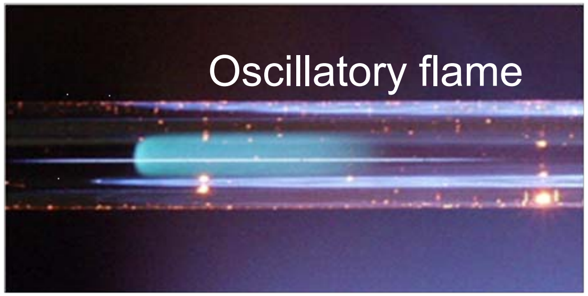
Stationary wall-temperature profile by an external heat source
Inner diameter of the tube < conventional quenching diameter
Gas phase temperature governed by wall temperature profile
Laminar flow and constant pressure

Flame behaviors in a micro flow reactor with a prescribed temperature profile

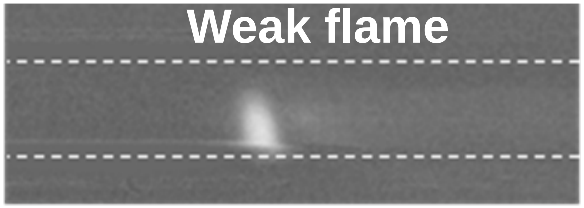



Normal flame

High velocity region

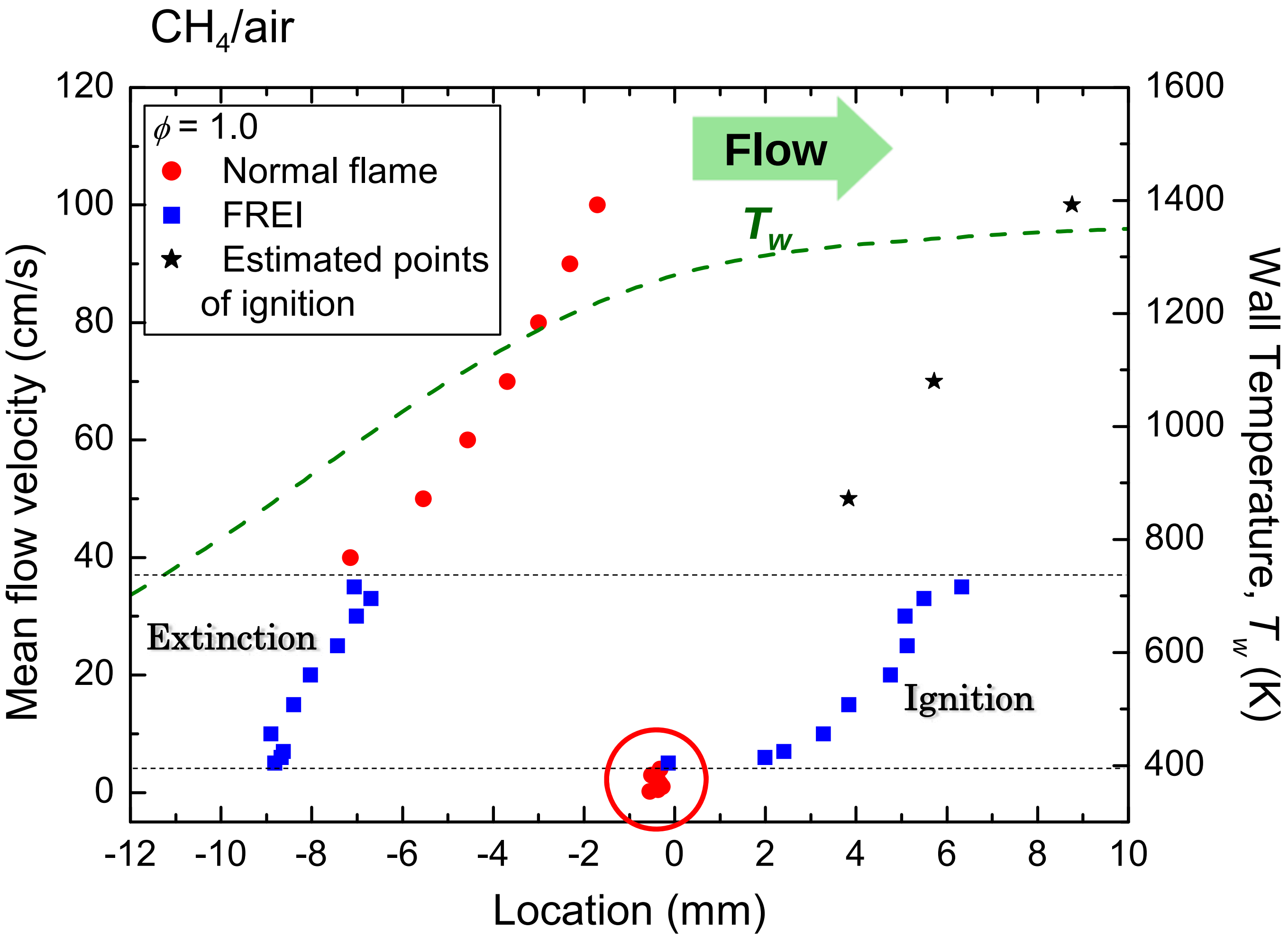

Oscillatory flame

Intermediate velocity region

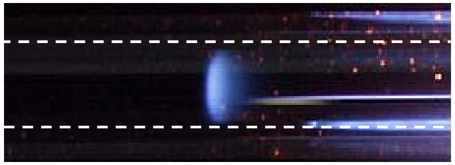


Low velocity region

Three kinds of flame responses

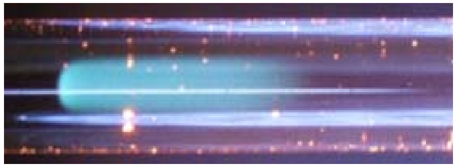


(1) Normal flame



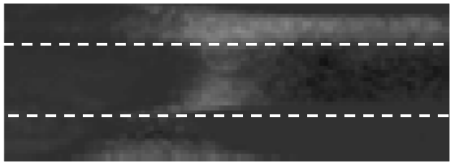
V=50cm/s

(2) Oscillatory flame



V=20cm/s

(3) Weak flame

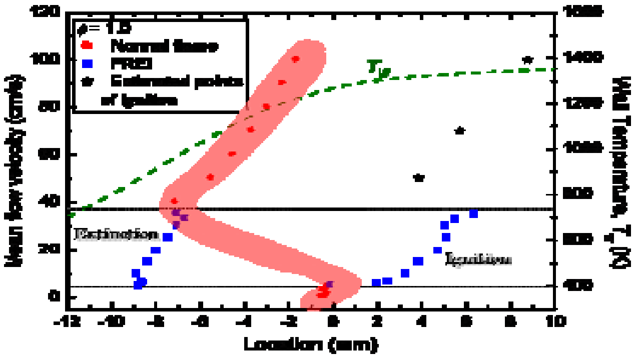


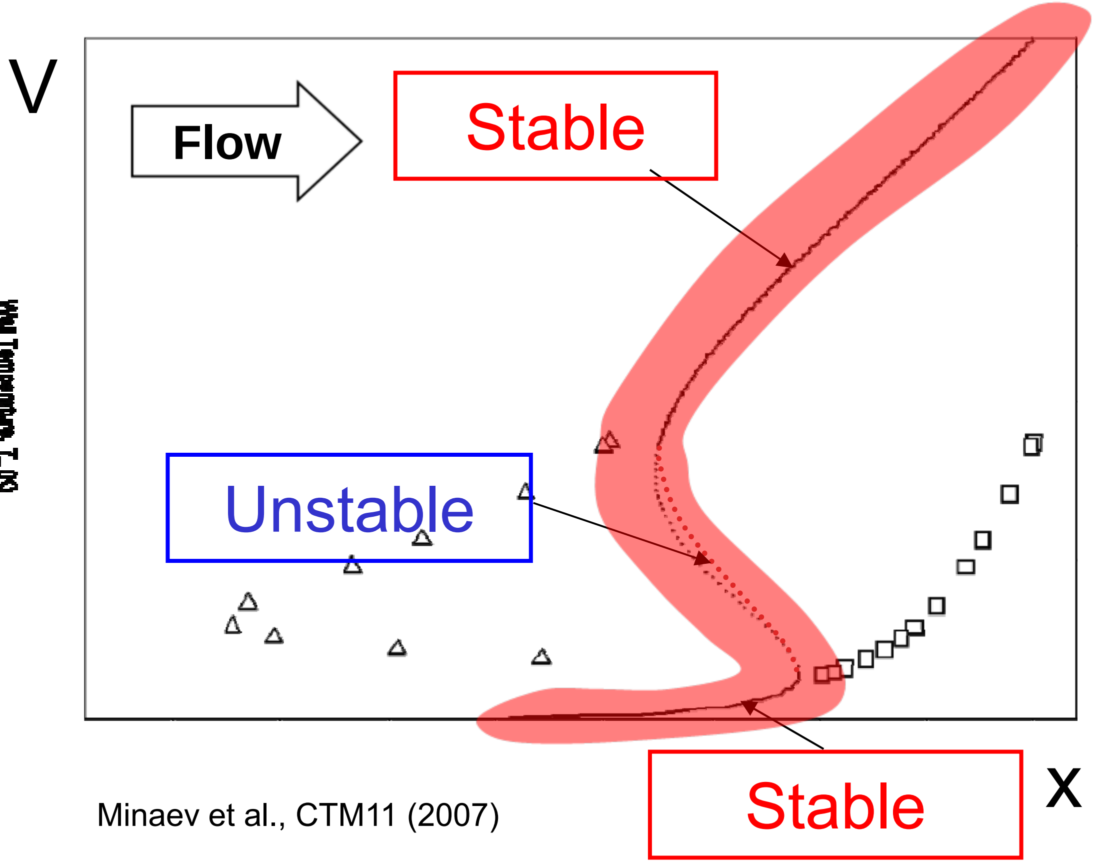
V=0.2cm/s

Normal flame, oscillatory flame, weak flame

Maruta et al., PCI30 (2005)

Theoretical S-shaped response

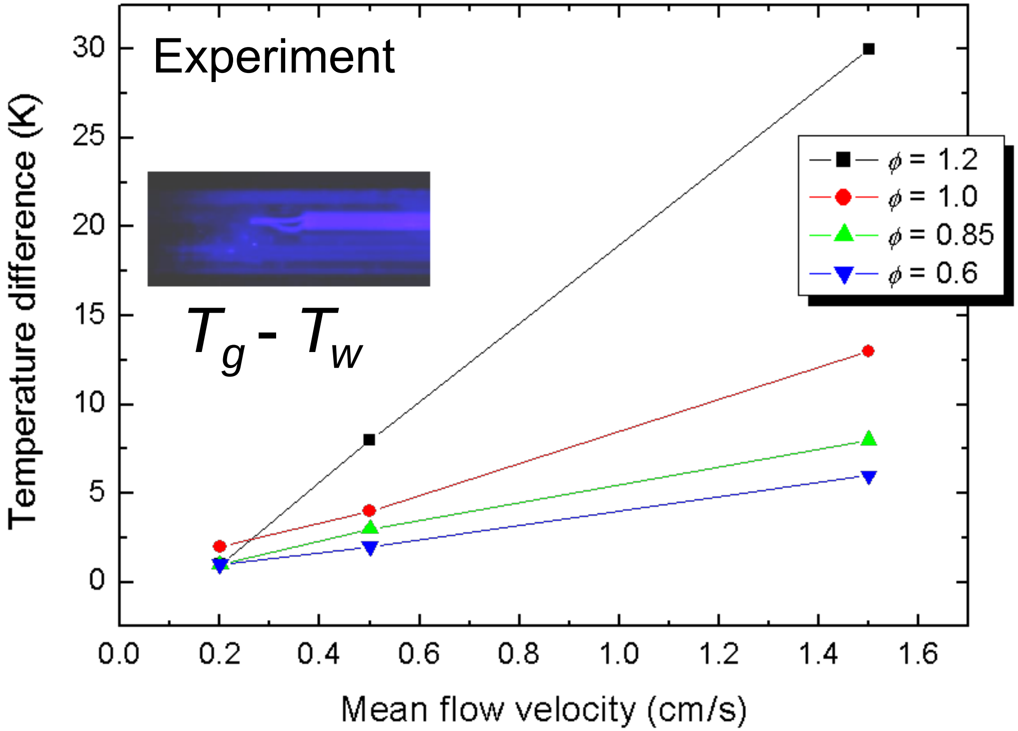




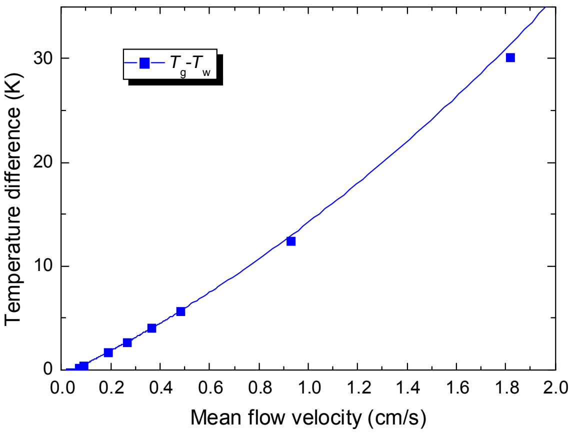
Minaev et al., CTM11 (2007)

Two stable and one unstable solutions predicted theoretically →
Weak flame corresponds to ignition branch

Lower limit of weak flames identified



Computation



At V = 0.2 cm/s, T_w = 1225 K, T_g-T_w< 2 K for CH_4/air mixture

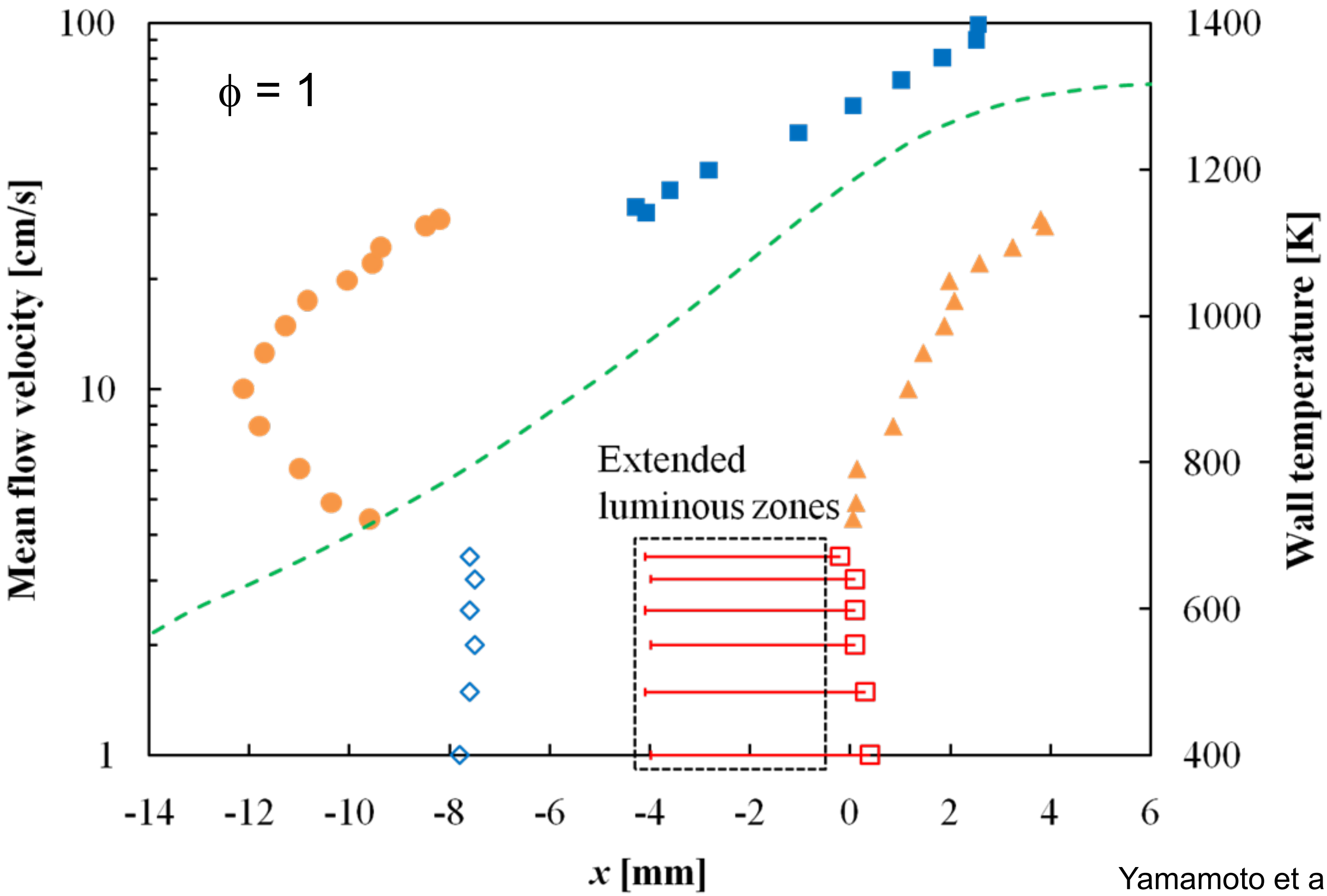
Extremely small temperature increase near lower limit

Flame position close to the ignition limit

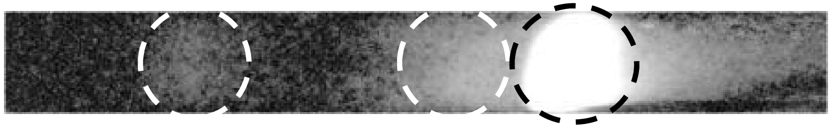
Weak flame location → Ignition temperature

Tsuboi et al., PCI32 (2009)

Triple weak flames, n-heptane



Yamamoto et al., PCI33 (2011)



U = 3 cm/s

Triple stationary weak flames observed
Weak flame location (temp.) insensitive to flow velocity

Computations (one-dimensional plug flow)

Code PREMIX with small modification

Gas-phase energy equation

$$\dot{M}\frac{dT}{dx}-\frac{1}{c_p}\frac{d}{dx}\left(\lambda A\frac{dT}{dx}\right)+\frac{A}{c_p}\sum_{k=1}^{K}\rho Y_k V_k c_{pk}\frac{dT}{dx}+\frac{A}{c_p}\sum_{k=1}^{K}\dot{\omega}_k h_k W_k\boxed{-\frac{A}{c_p}\frac{4\lambda Nu}{d^2}(T_w-T)}=0$$

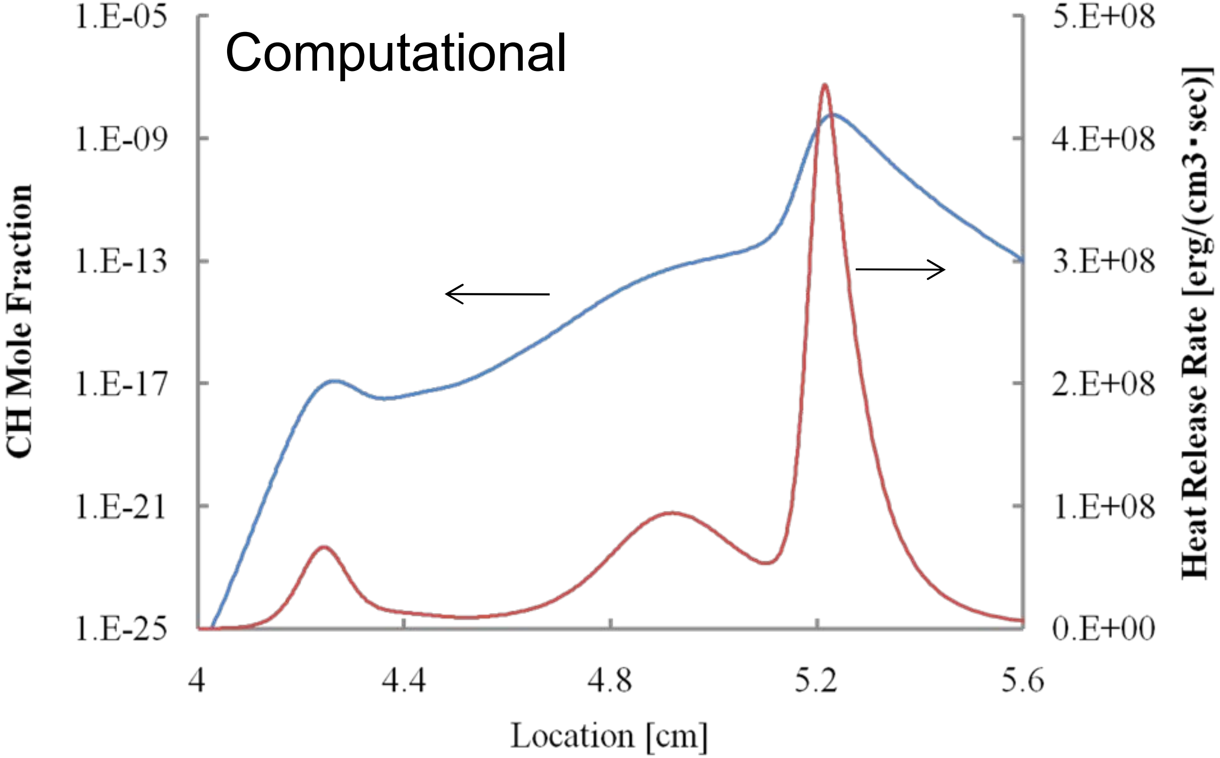
Heat transfer with the wall

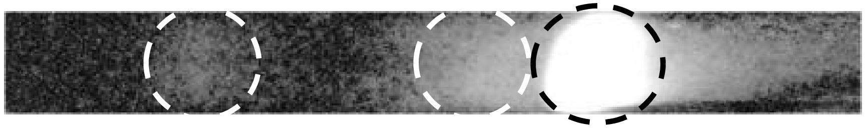
Reaction scheme *n*-heptane, reduced mechanism from LLNL
(159 species, 1540 steps) Seiser et al., PCI 28 (2000)

Conditions Stoichiometric gaseous *n*-heptane/air mixture
Experimental wall temperature profile was provided as Tw(x)

Flame position Peaks of heat-release-rate (HRR) [W/cm^3] profile

Triple weak flames, n-heptane

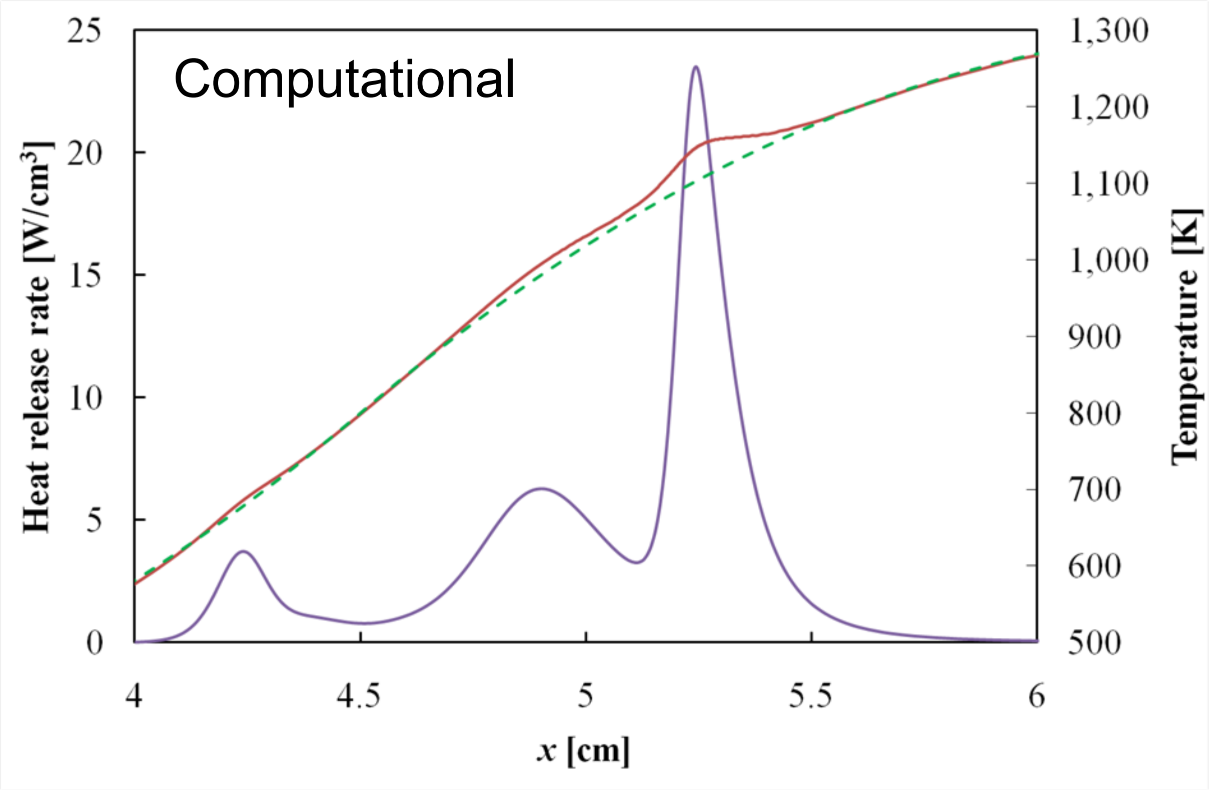


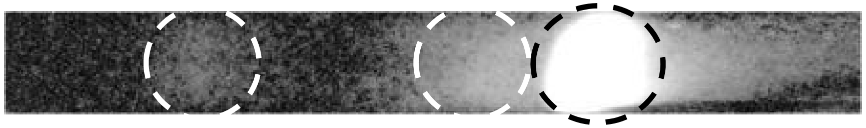


U = 3 cm/s

Three-stage heat release

Triple weak flames, n-heptane

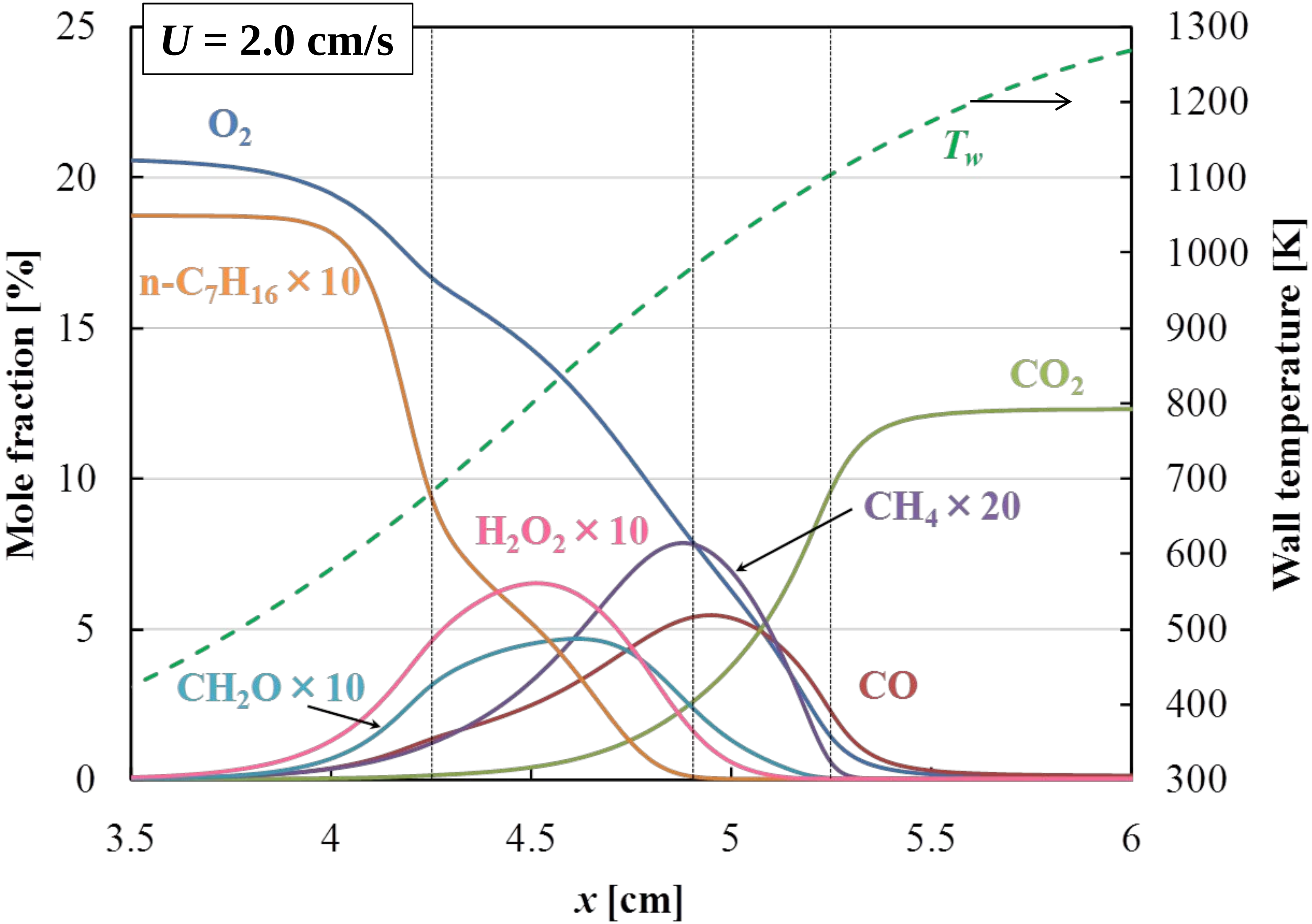




U = 3 cm/s

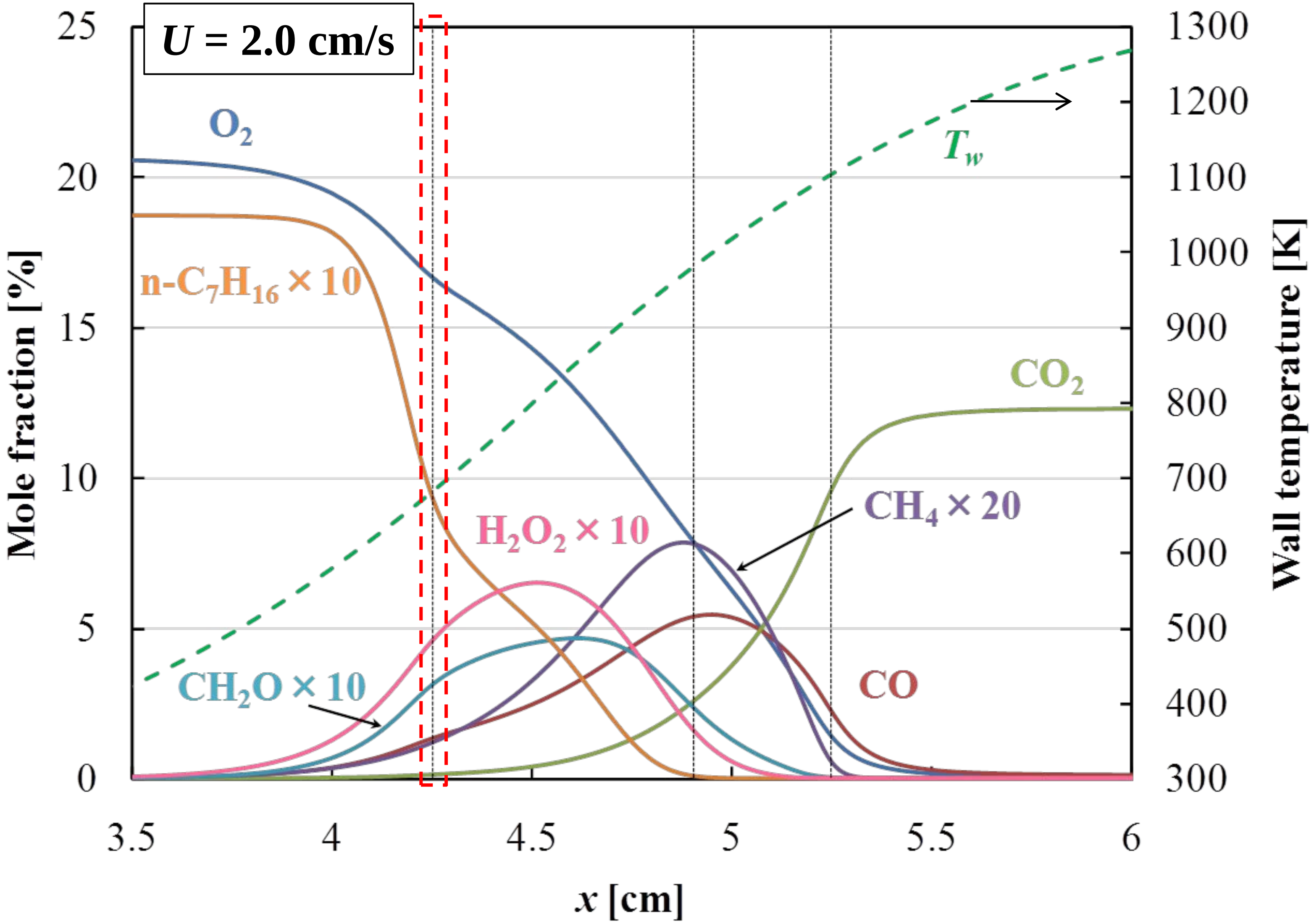
Three-stage heat release

Computational species profiles



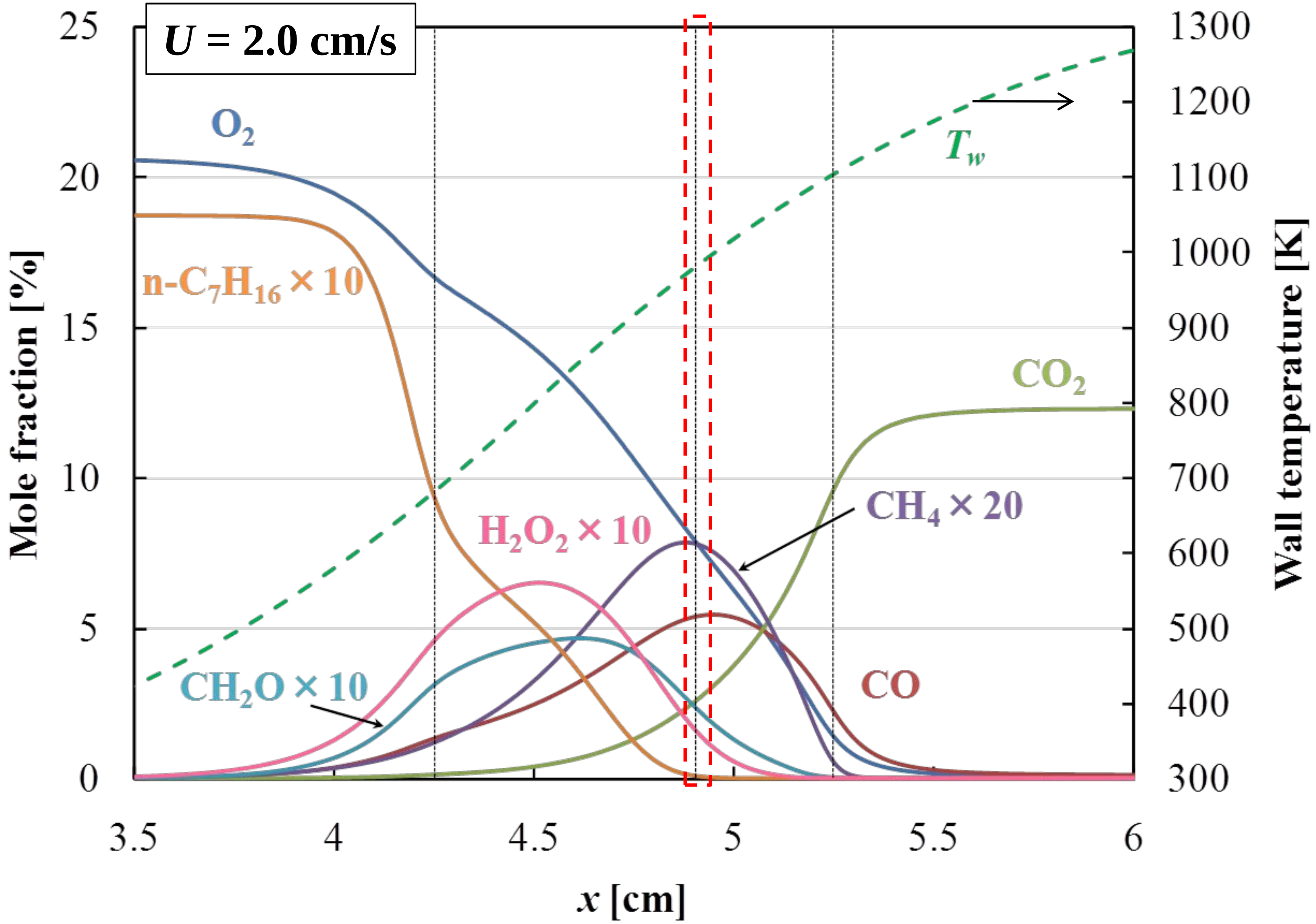
Yamamoto et al., PCI33 (2011)

Computational species profiles -1st weak flame-



LTO: CH_2O, H_2O_2, CO, CH_4 produced

Computational species profiles -2nd weak flame-



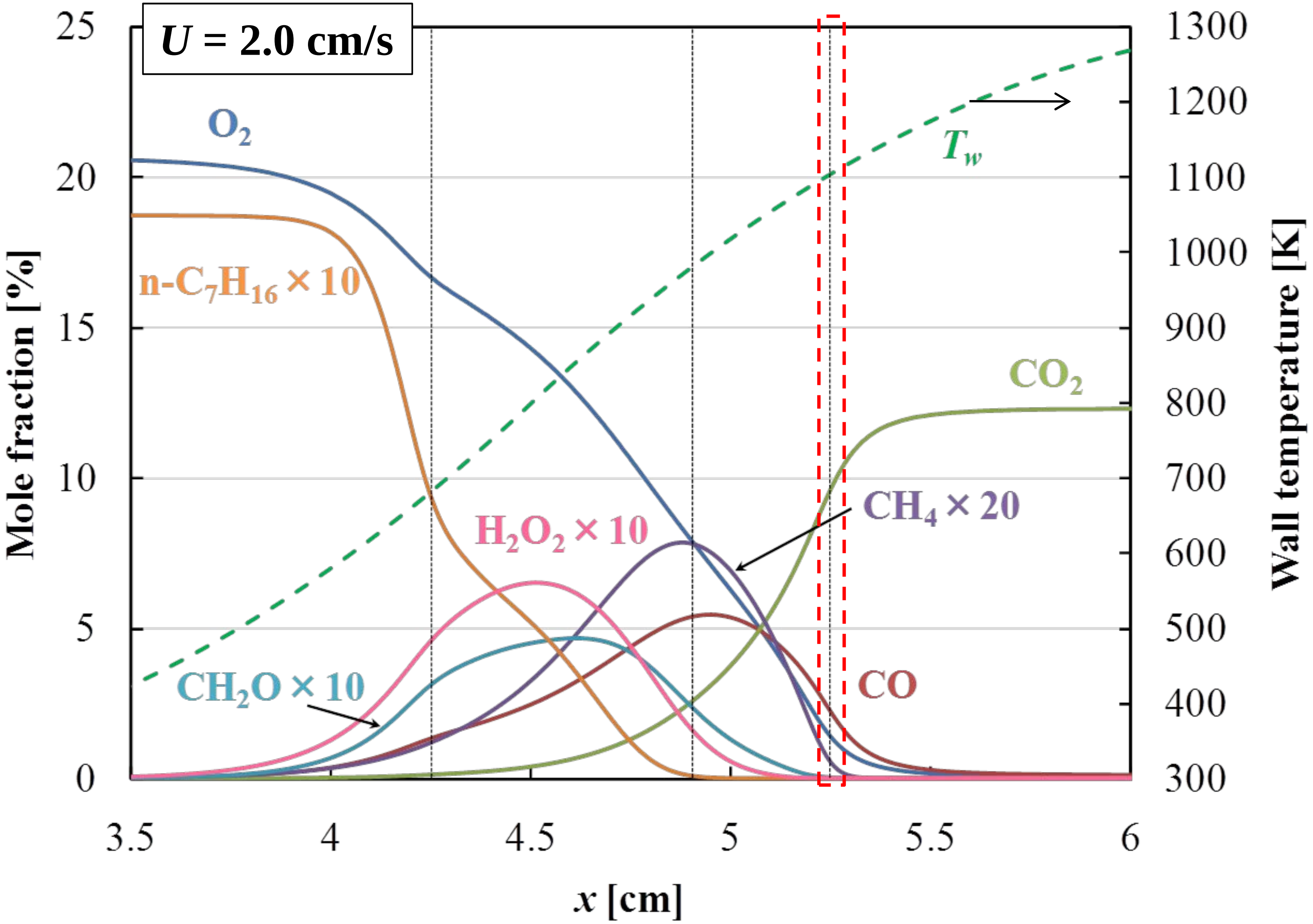
Partial oxidations:

$\mathbf{H_2O_2}$ (+M) ⇒ 2OH (+M)

$\mathbf{CH_2O} + OH \Rightarrow \underline{HCO} + H_2O$

$\underline{HCO} + O_2 \Rightarrow \mathbf{CO} + HO_2$

Computational species profiles -3rd weak flame-

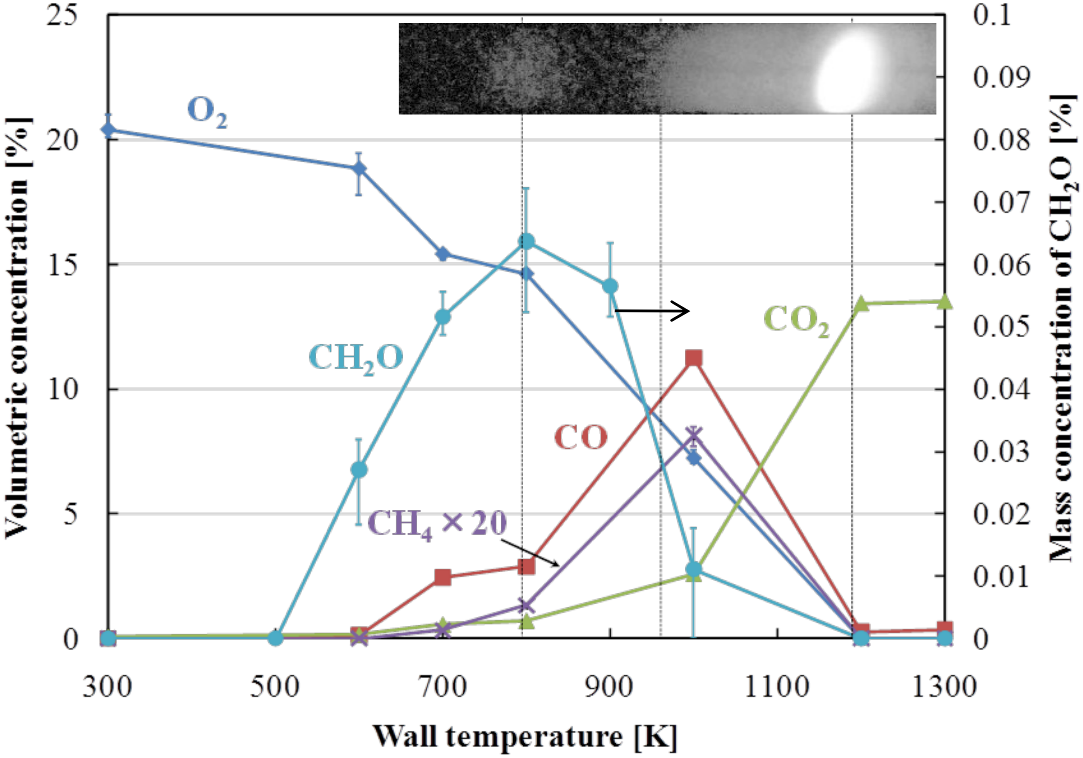


Full oxidations: $\mathbf{CO} + OH \Rightarrow \mathbf{CO_2} + H$

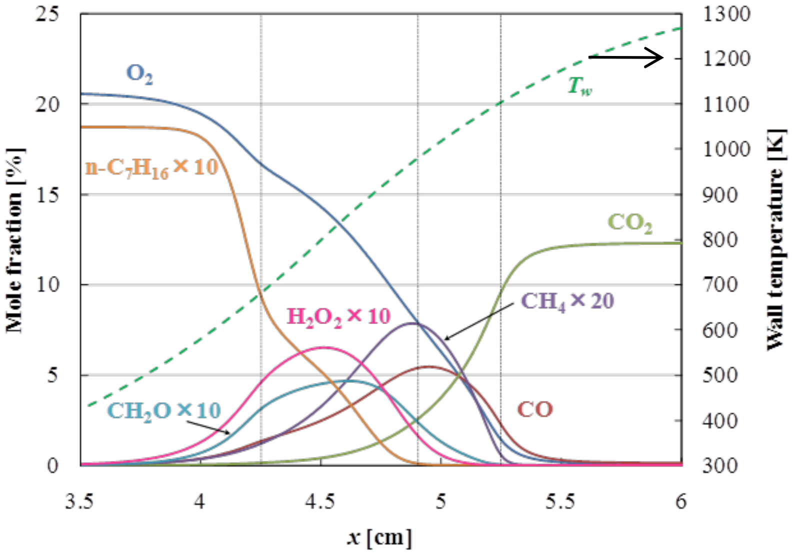
Comparison: measurements and computations

(U = 2.0 cm/s)

Measurement by GC



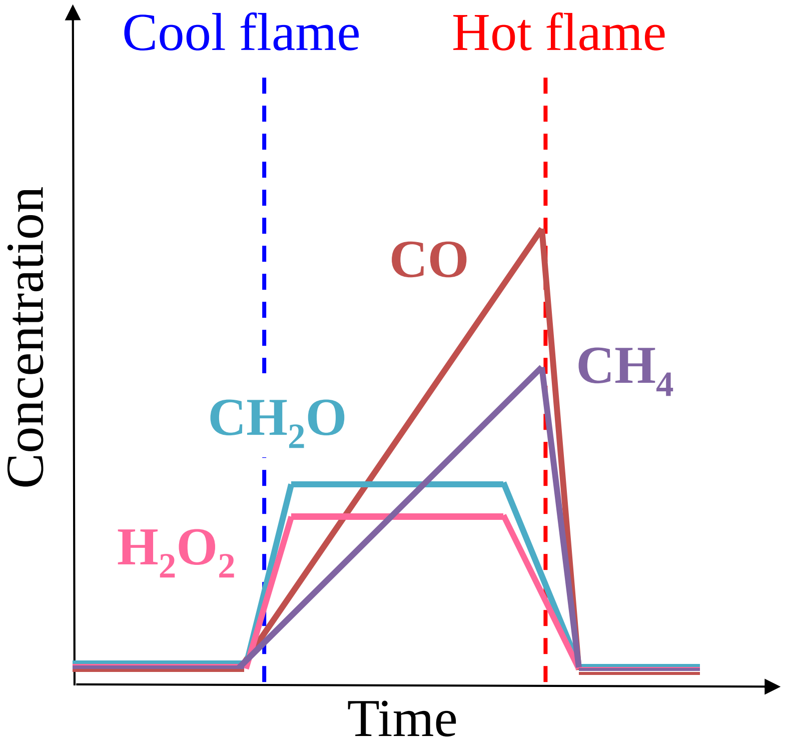
Computations



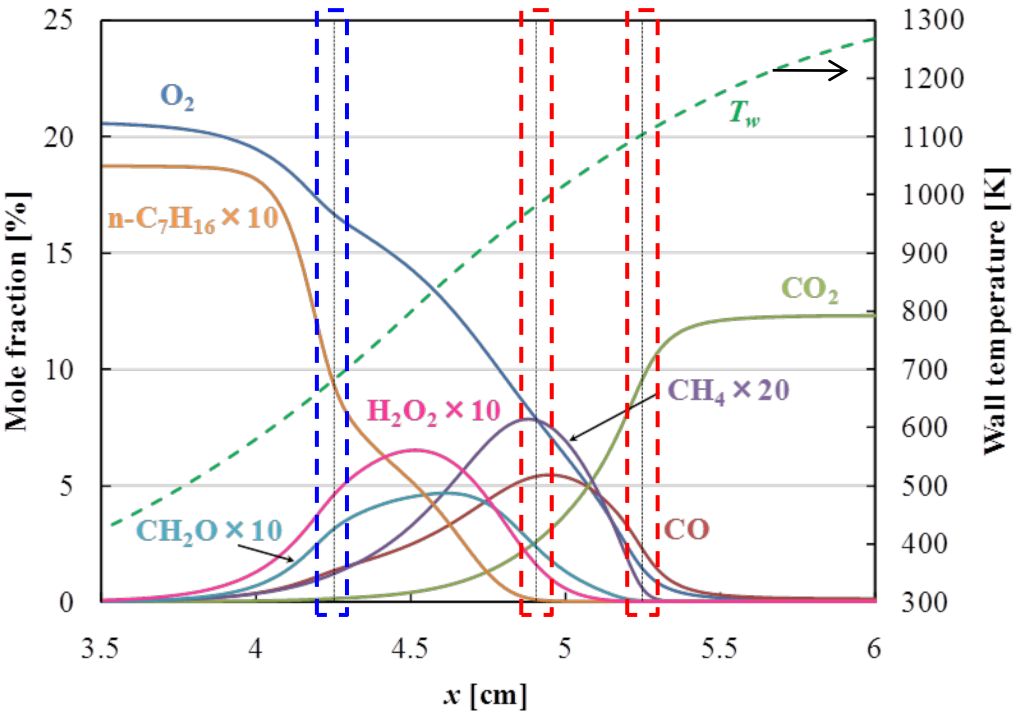
Three-stage oxidation process was experimentally confirmed by gas sampling

Interpretation of triple weak flames in MFR

Typical two-stage oxidation



Present three-stage oxidation



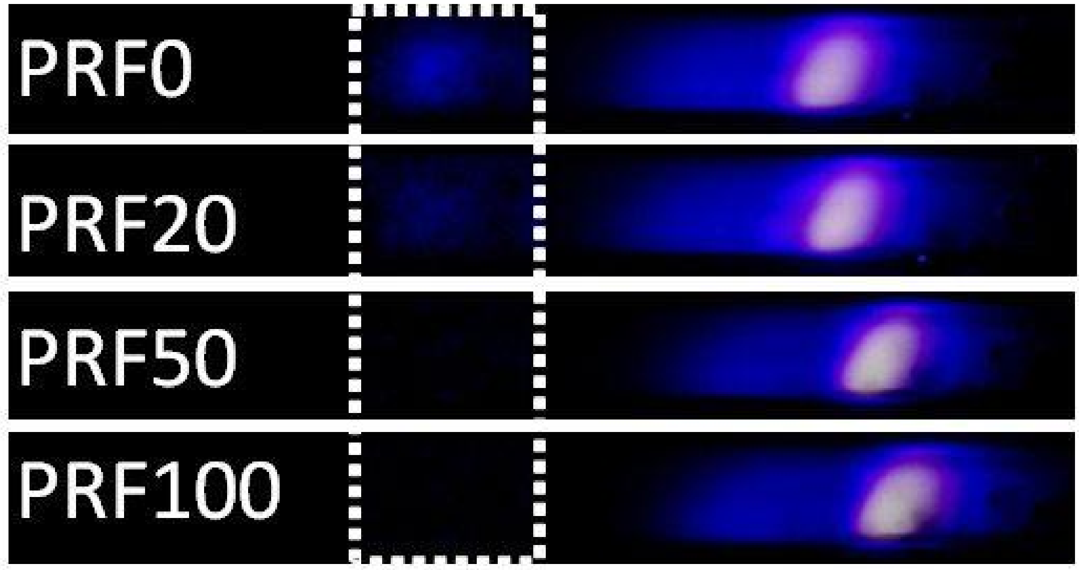
Typical two-stage oxidation: Cool flame + Hot flame

Three-stage oxidation: Cool flame + Separated hot flames

(Blue flame & Hot flame)

MFR applied for gasoline PRF

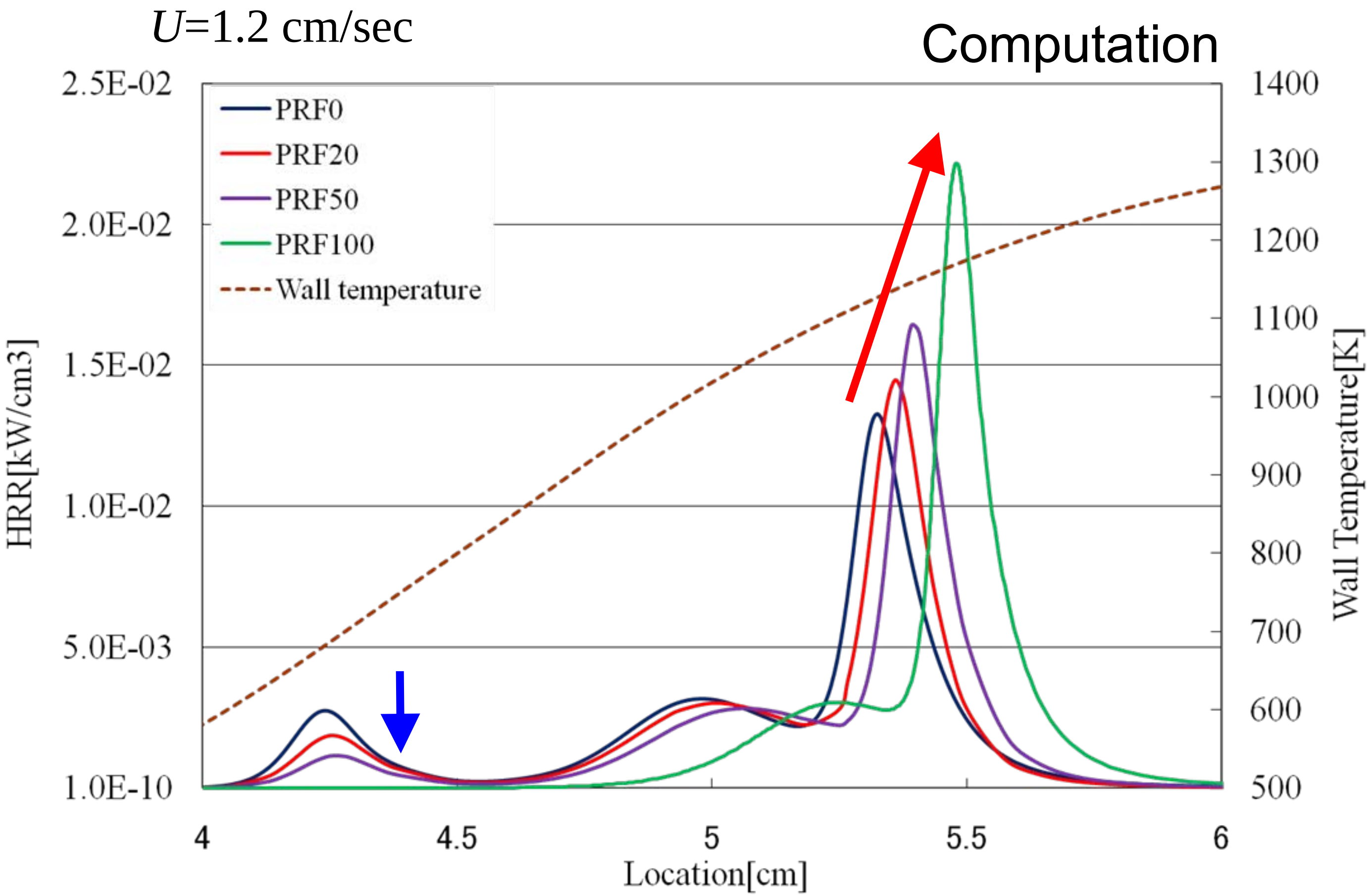
n-heptane + *iso*-octane (PRF)


PRF0
PRF20
PRF50
PRF100

Appearances of multiple weak flame represent Research Octane Number

Hori et al., CNF159 (2012)

Weak flames at different RON

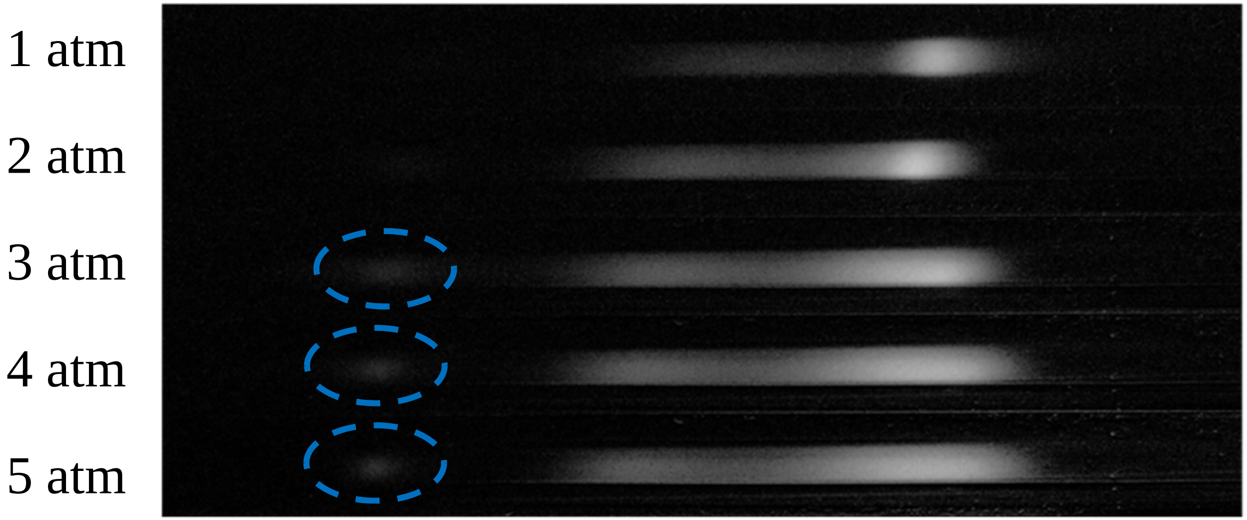


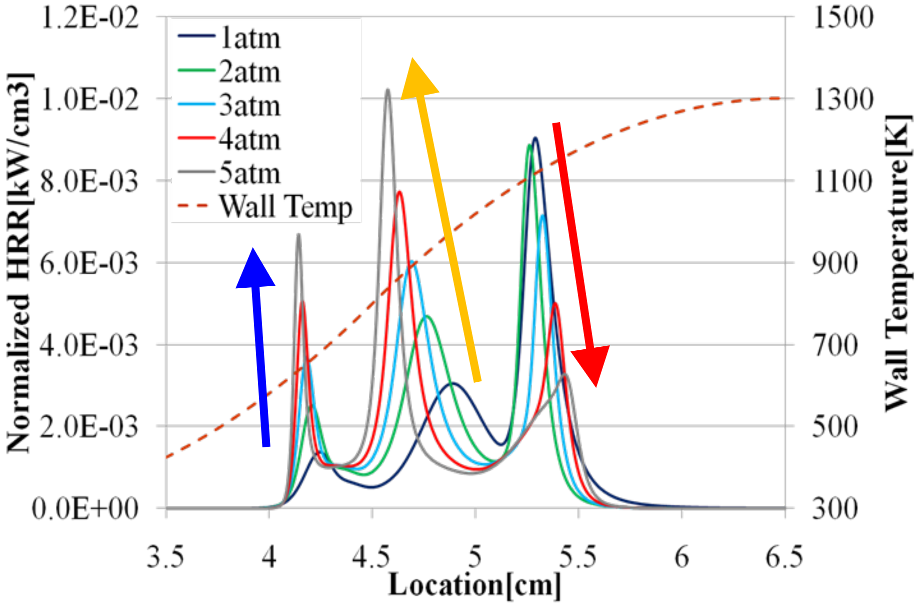
Significant LTO in smaller RON

Weak flame behaviors reproduced

Weak flames at elevated pressures

PRF0 / air, *U*=2.0 cm/sec


1 atm
2 atm
3 atm
4 atm
5 atm



PRF20, 50, 100 similar Tendencies but weaker LTO

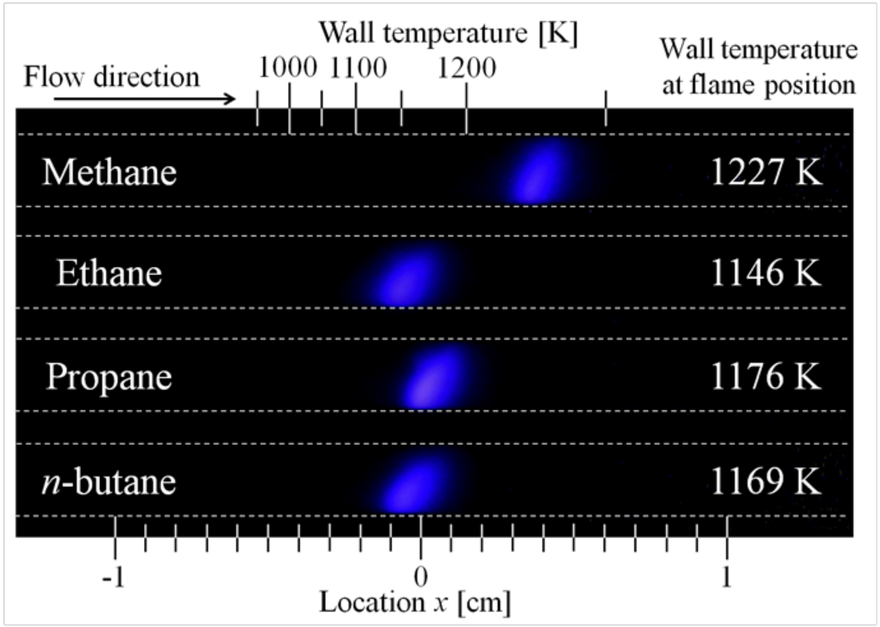
Hori et al., CNF159 (2012)

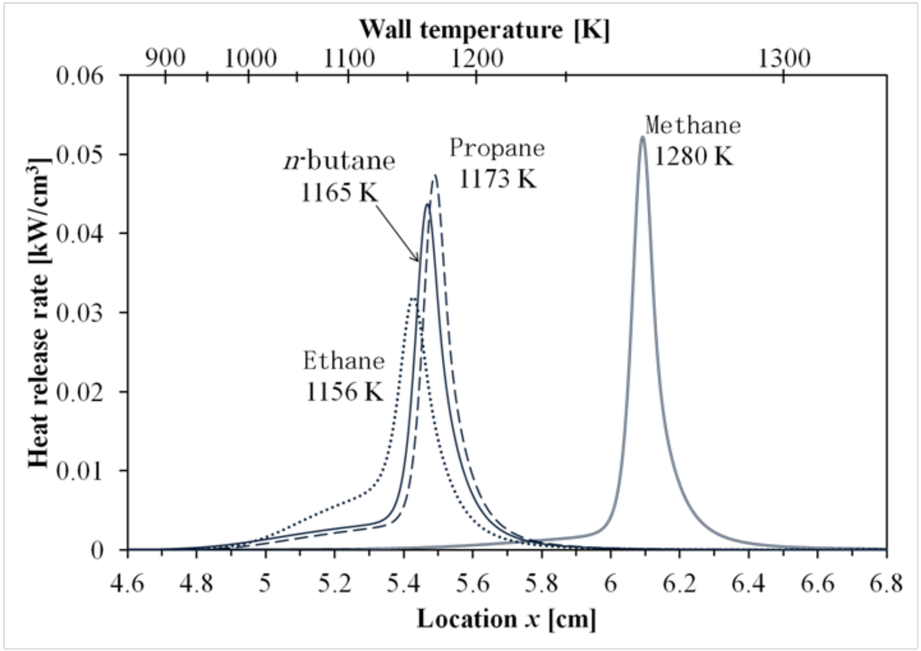
Fuels addressed

methane (CH_4)
↓
DME (CH_3OCH_3)
↓
n-heptane (C_7H_{16})
iso-octane (C_8H_{16})
toluene (C_7H_8 or $C_6H_5CH_3$)
↓
methane (CH_4)
ethane (C_2H_6)
propane (C_3H_8)
n-butane, *iso*-butane (C_4H_{10}) → (Kamada et al., WIPP)

Natural gas components

(Kamada et al., WIPP)

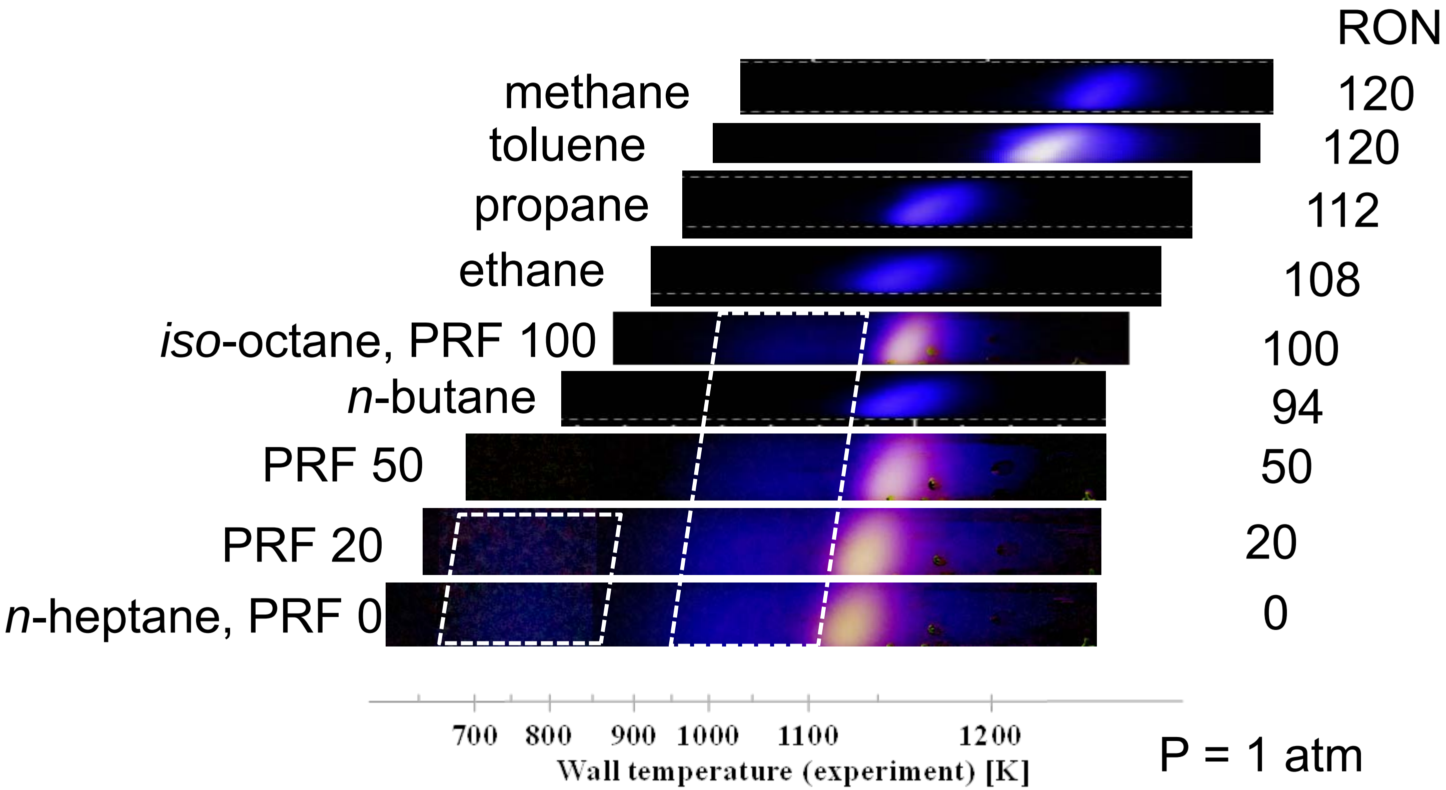

Wall temperature [K]
Flow direction
1000
1100
1200
Wall temperature at flame position
Methane
1227 K
Ethane
1146 K
Propane
1176 K
n-butane
1169 K
-1
0
1
Location *x* [cm]



Similar single weak flame (hot flame) observed for each fuel
Different flame locations
Computations reproduced experimental observation

Weak flames at various RON

Data collected at slightly different conditions,
i.e., flow velocity, exposure time, temperature profile



P = 1 atm

3rd weak flame (main flame) location (temp.) monotonic function of RON
2nd weak flame (blue flame) observable when RON < 100
1st weak flame (cool flame) observable when RON < 20

Conclusions and future, 1 of 2

Micro flow reactor with prescribed temperature profile was introduced

-Three kinds of flame response (S-shaped)

-Weak flame corresponds to ignition branch

-Multiple weak flame utilized for fuel characterization

-Multiple weak flames at elevated pressures

-Appearances of weak flame correlated with RON

Conclusions and future, 2 of 2

Diesel fuels and Cetane numbers

n-cetane (hexadecane, $C_{16}H_{34}$)
iso-cetane (2,2,4,4,6,8,8-heptamethylnonane, $C_{16}H_{34}$)
n-decane ($C_{10}H_{22}$)
α-methylnaphthalene ($C_{11}H_{10}$) → (Suzuki et al., 5E06)

Ethanol → (Nakamura et al., 1E02)
Syngas
Oxyfuel combustion → （Li et al., WIPP)
Effect of surface reaction → (Kizaki et al, WIPP)
PAH and soot

Optical diagnosis

LIF, CRDS for precise species profile measurements

Higher pressures

High pressure chamber (up to 20 bar) fabricated

Acknowledgements

IHI, IIC, HONDA R&D, JAXA, NEDO, HITACHI, TG, MEXT

Micro
Flow
Reactor

Micro flow reactor now commercially available

Predictive Theoretical Elementary Reaction Kinetics and its Role in Combustion Modeling

Stephen J. Klippenstein

Theoretical Elementary Reaction Kinetics

Potential Energy Surface Exploration

- Ab Initio Electronic Structure Theory
- Stationary Points – Minima and Transition States
- Evaluate Energies and Rovibrational Properties

Predict Rate Constants for Individual Dynamical Steps

- Transition State Theory (TST)
- Evaluate Partition Functions
- Tunneling, Hindered Rotors, Variational Effects

Predict Collision Induced Energy Transfer Rates

- Collision Rate
- Energy Transfer Distribution
- Usually Empirical

Predict/Model Pressure Dependence

- Master Equation -> Population vs. Time
- Represent with Kinetic Phenomenology

Team Effort

How to Calculate Rate Constants Accurately and Efficiently?

Ab Initio **Transition State Theory** **Master Equation**

Lawrence B. Harding Yuri Georgievskii James A. Miller

AITSTME Coding Team

Energy Transfer

Ahren Jasper

Applications

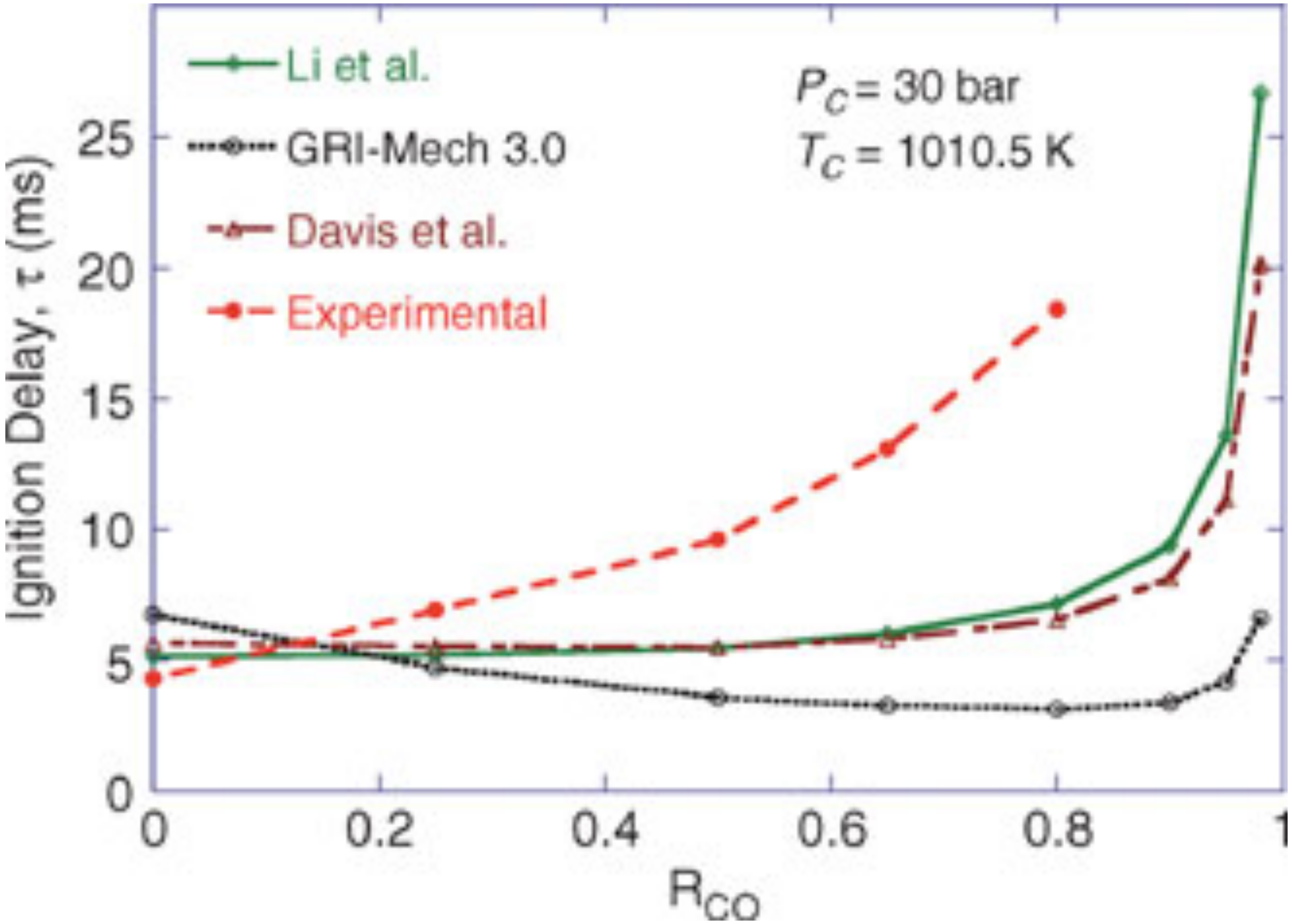
Judit Zador

Outline

1. Theoretical Studies Motivated by Modeling
    - $CO + HO_2$, $H + HO_2$, $CH_3OH + HO_2$
    - NNH Chemistry
    - $CH_2 + O_2$
    - $C_3H_6OOH + O_2$
    - C_4H_9OH, C_4H_9O, $C_4H_9O + O_2$

2. Uncertainties
    - Electronic Energies
    - Vibrational Frequencies
    - Torsional Modes
    - Energy Transfer
    - Coupling of TST and Energy Transfer

$CO/H_2/O_2$ Oxidation: Ignition Delays in RCM

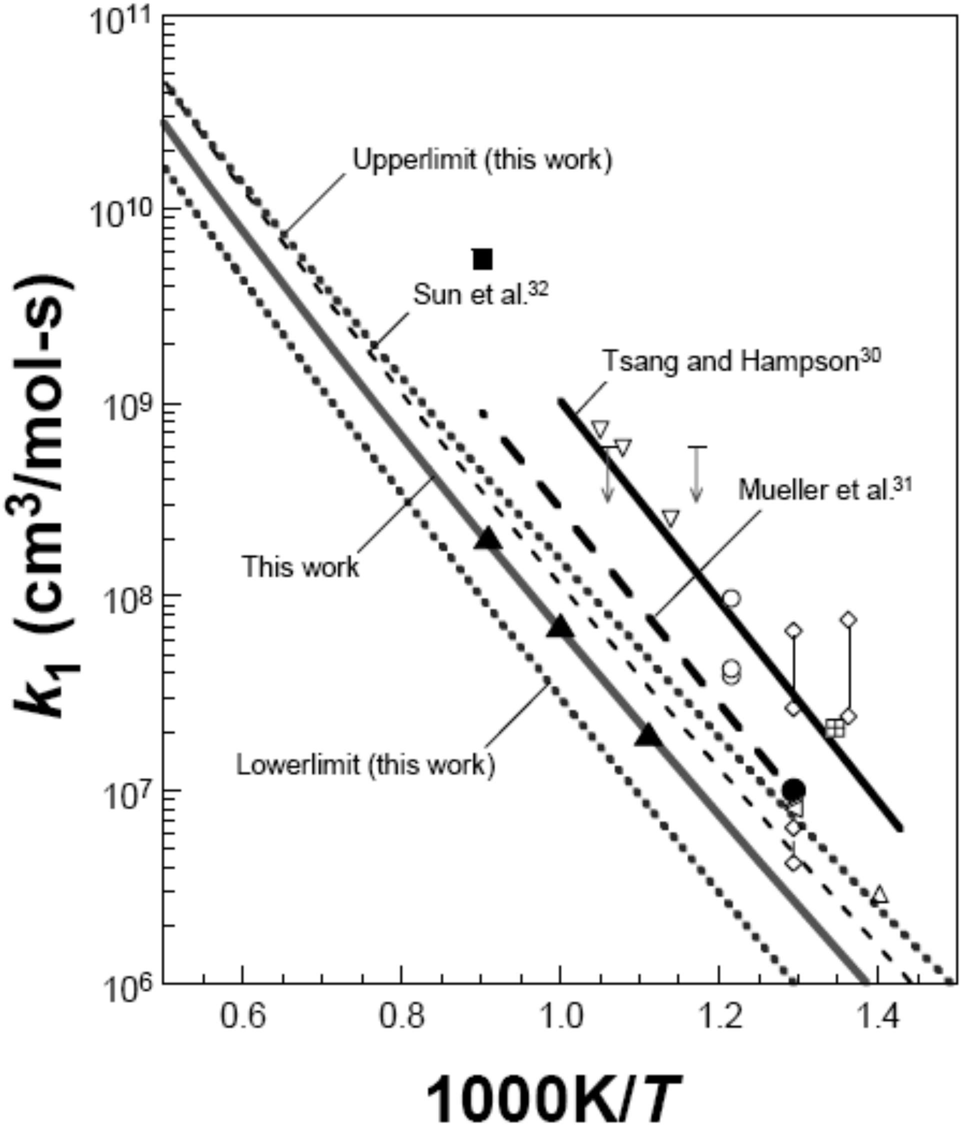


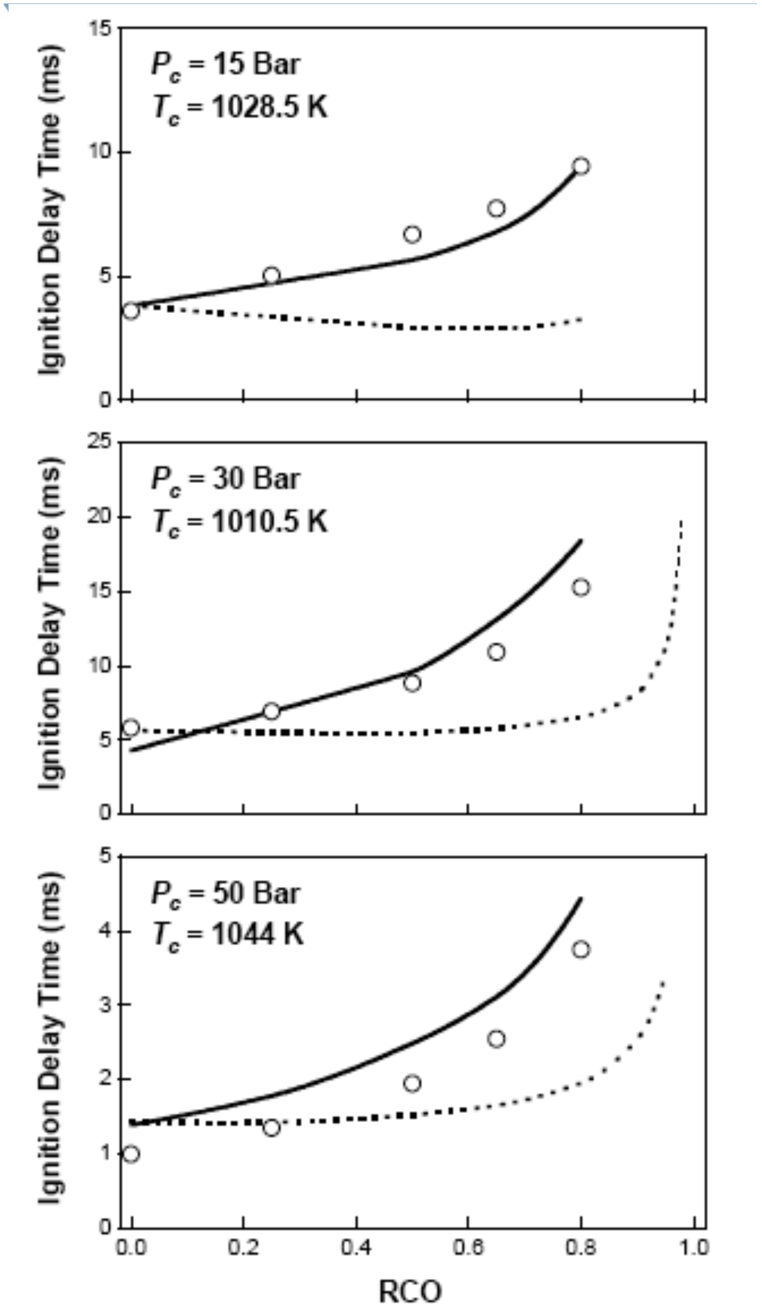
G. Mittal, C. J. Sung, R. A. Yetter, Int. J. Chem. Kinet. 38, 516 (2006).

Uncertainty Analysis Highlighted Sensitivity to $CO + HO_2$

G. Mittal, C. J. Sung, M. Fairweather, A. S. Tomlin, J. F. Griffiths, K. J. Hughes, Proc. Comb. Inst. 31, 419 (2007).

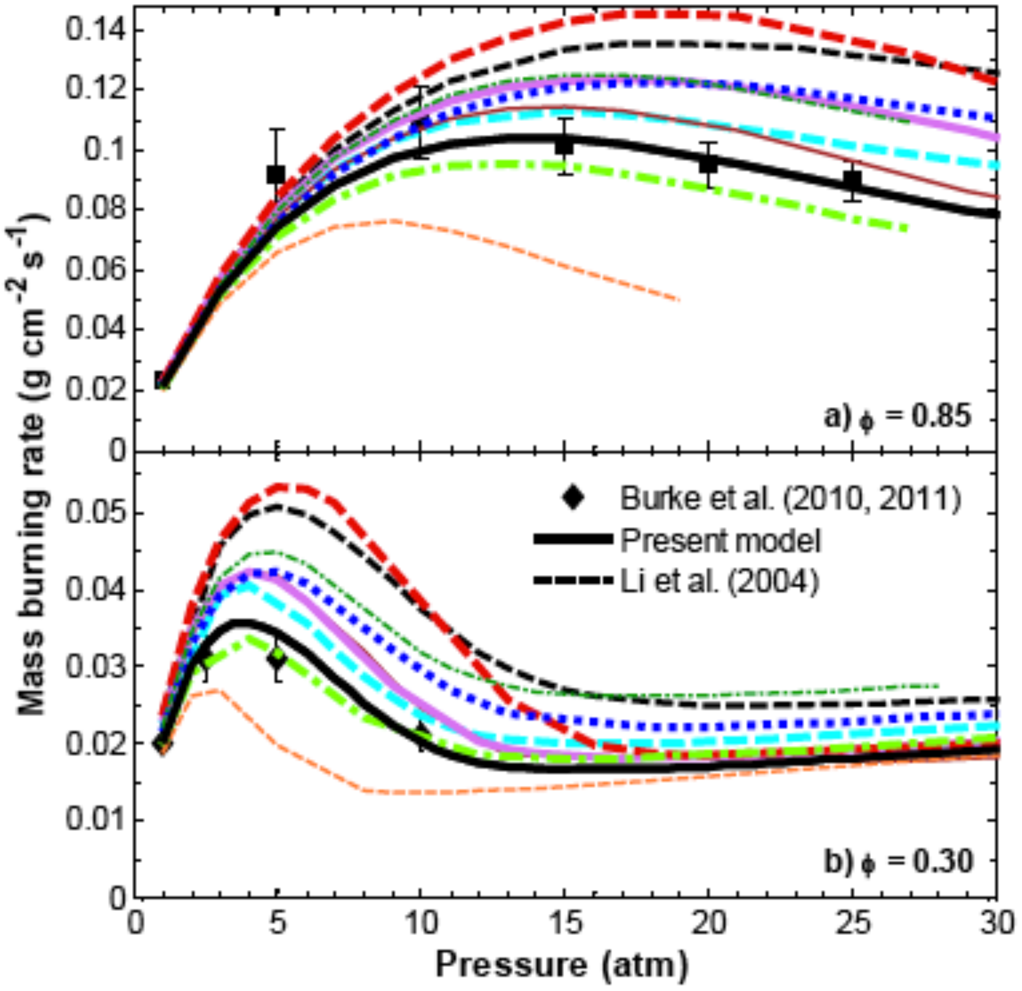
$CO + HO_2 \rightarrow CO_2 + OH$

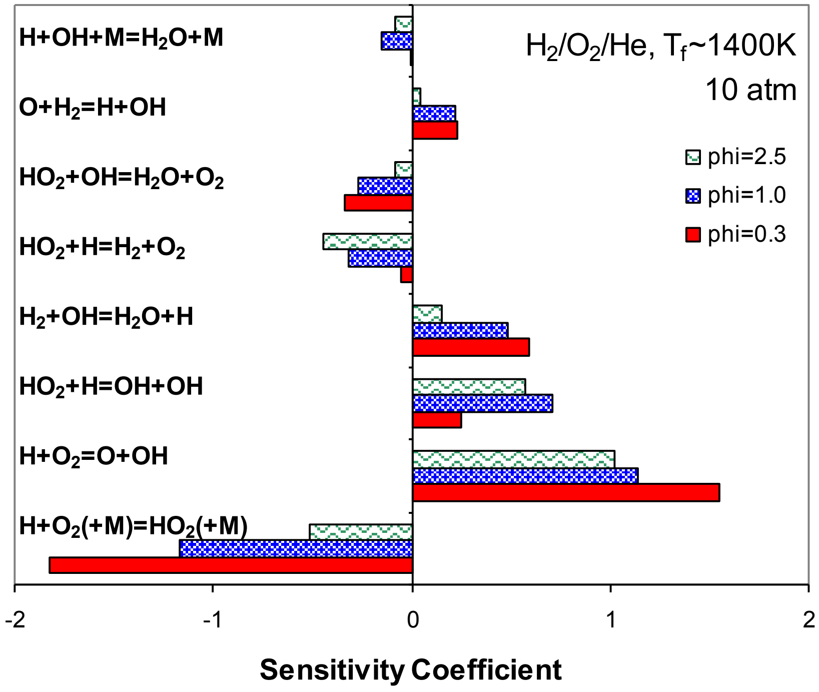


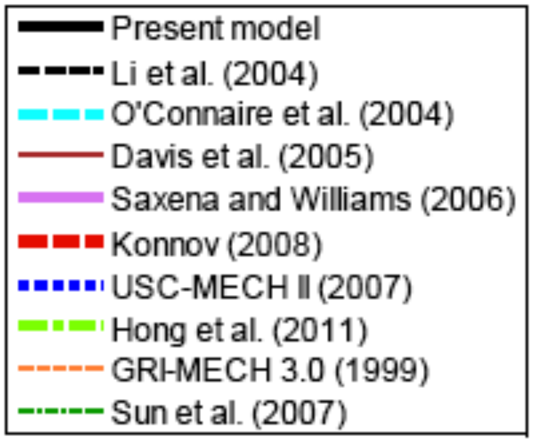


You, Wang, Goos, Sung, Klippenstein, J. Phys. Chem. A, 111, 4031 (2007)

H_2/O_2 at High Pressure

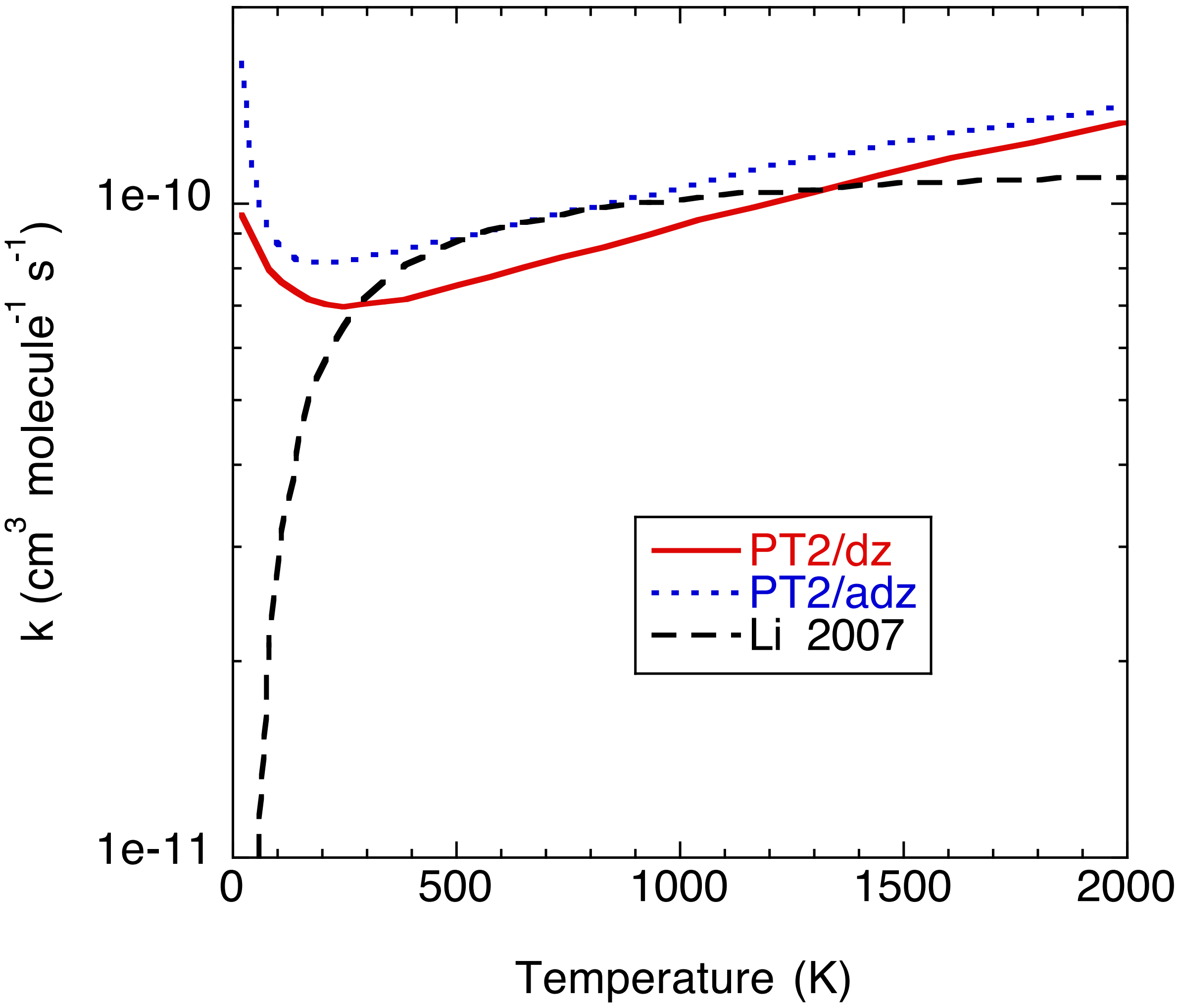






Burke, Chaos, Ju, Dryer, Klippenstein, Int. J. Chem. Kinet. 44, 444 (2012).

H + HO_2 Recombination



Direct CASPT2 Variable Reaction Coordinate TST Calculations

~ 20% Uncertainty

Validate Modeling Determined Rate

The Role of NNH in NO Formation and Control

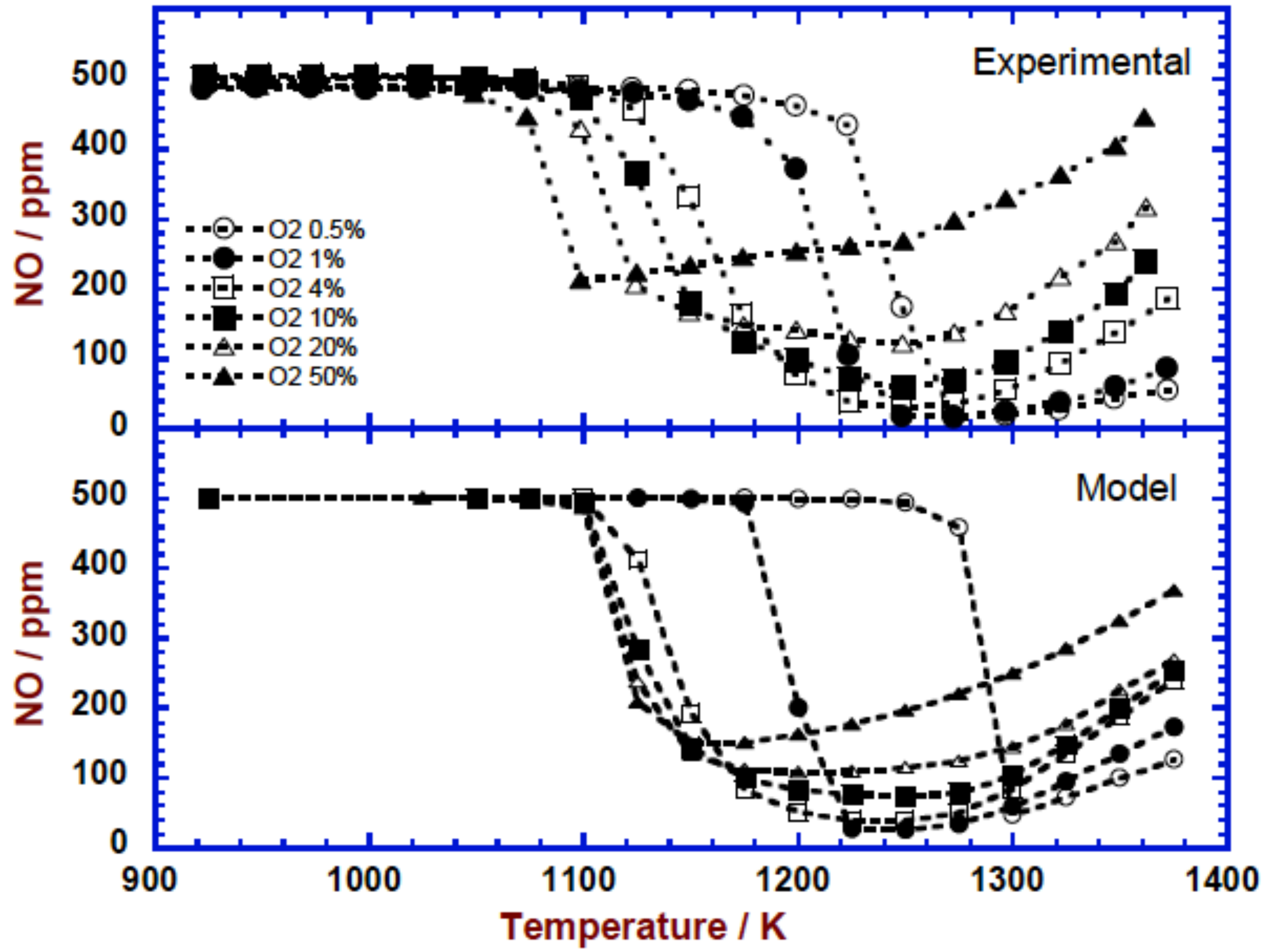
NNH Lifetime – Discrepancy between value required for modeling and value predicted by theory

NNH Mechanism for NO_x Formation – Possibly important at low temperatures

1. $NNH + O_2$
2. $NNH + O$; $NH + NO$, $H + N_2O$
3. $NH_2 + O_2 \rightarrow H_2NO + O$
4. Literature Review of NNH Lifetime and Thermochemistry
5. More accurate branching ratios for $NH_2 + NO$

S. J. Klippenstein, L. B. Harding, P. Glarborg, and J. A. Miller, Comb. Flame, 158, 774 (2011).

Modeling vs Expt NO O_2 and T Dependence

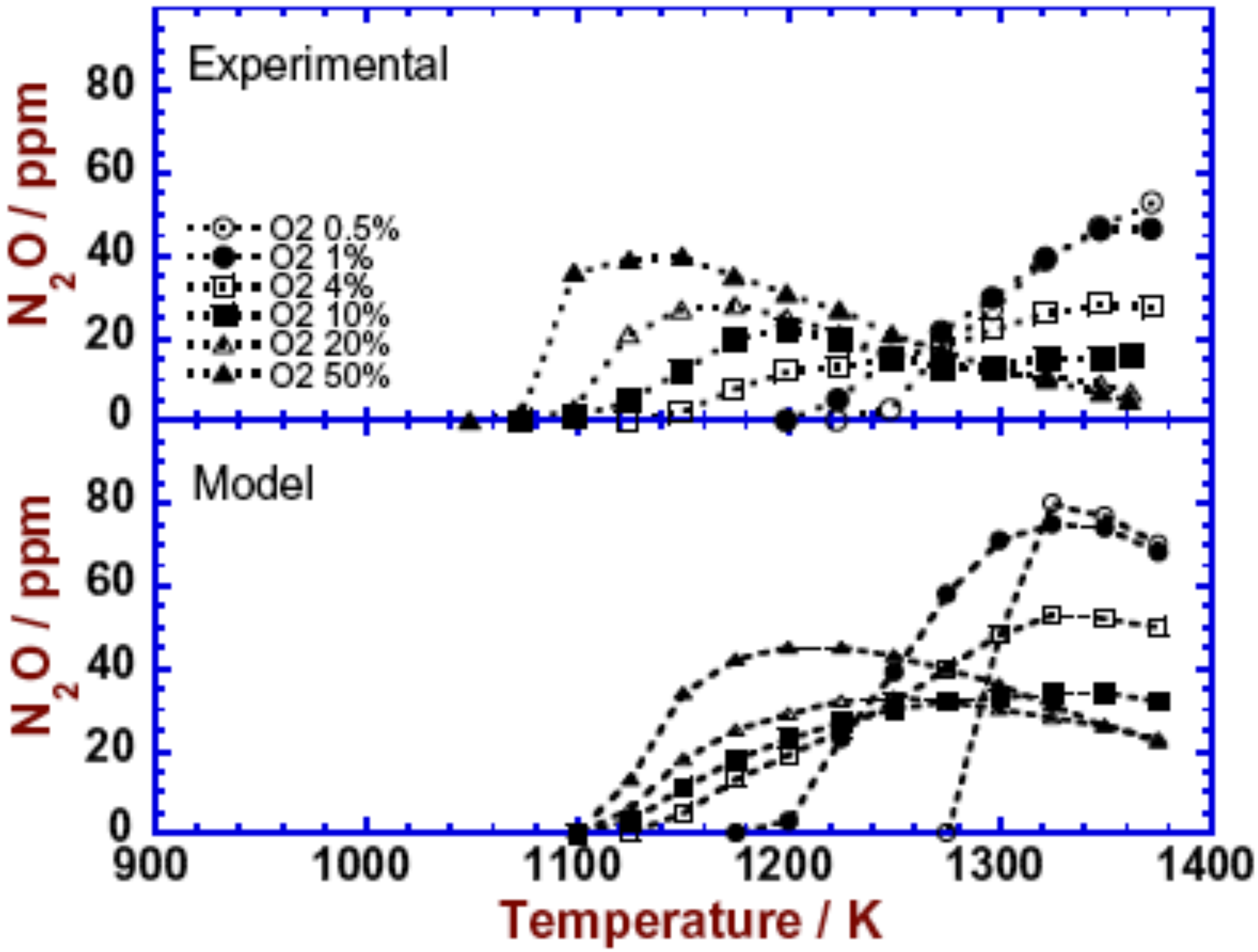


Experiments:
F. Kasuya, P. Glarborg, K. Dam-Johansen, Chem. Eng. Sci. 50 (1995) 1455-1466.

Modeling vs Expt N_2O O_2 and T Dependence

Inlet concentrations:
NO = 500 +/- 30 ppm
NH_3 = 1000 +/- 60 ppm
H_2O = 5%
balance N_2

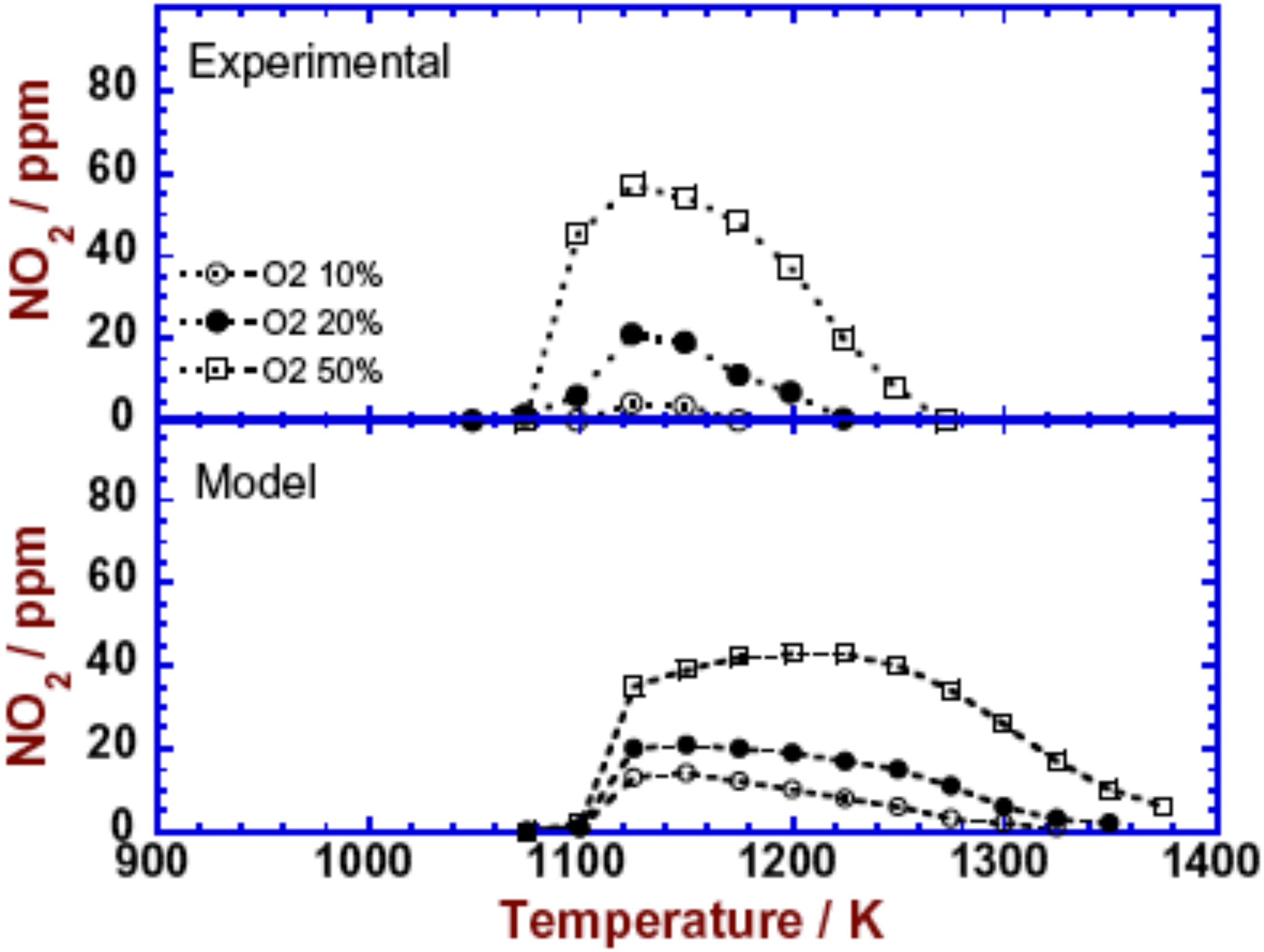
F. Kasuya, P. Glarborg, K. Dam-Johansen, Chem. Eng. Sci. 50 (1995) 1455-1466.



Modeling vs Expt NO_2 O_2 and T Dependence

Inlet concentrations:
NO = 500 +/- 30 ppm
NH_3 = 1000 +/- 60 ppm
H_2O = 5%
balance N_2

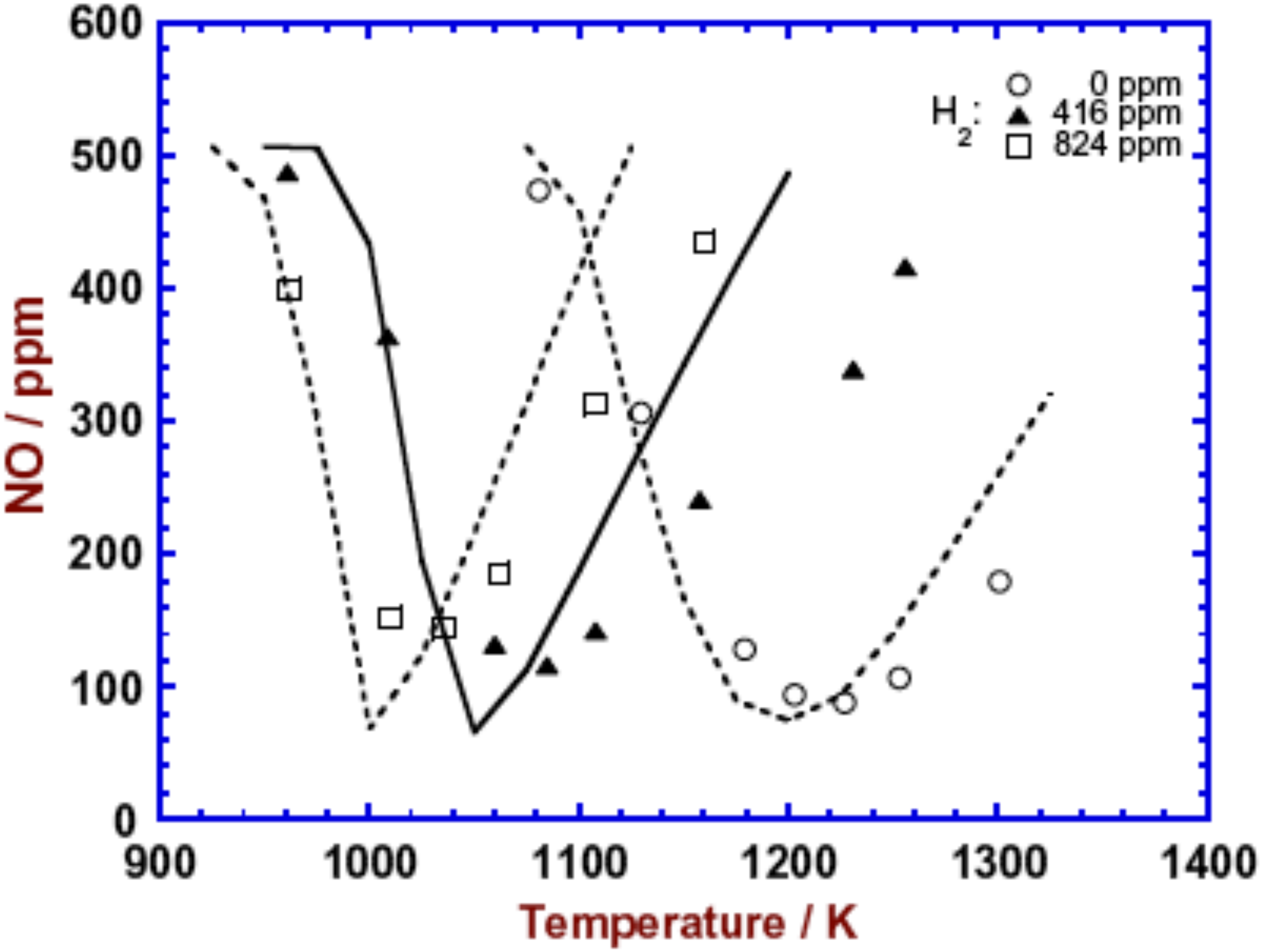
F. Kasuya, P. Glarborg, K. Dam-Johansen, Chem. Eng. Sci. 50 (1995) 1455-1466.



Modeling vs Expt NO H_2 and T Dependence

Inlet concentrations:
NO = 500 +/- 30 ppm
NH_3 = 1000 +/- 60 ppm
H_2O = 5%
balance N_2

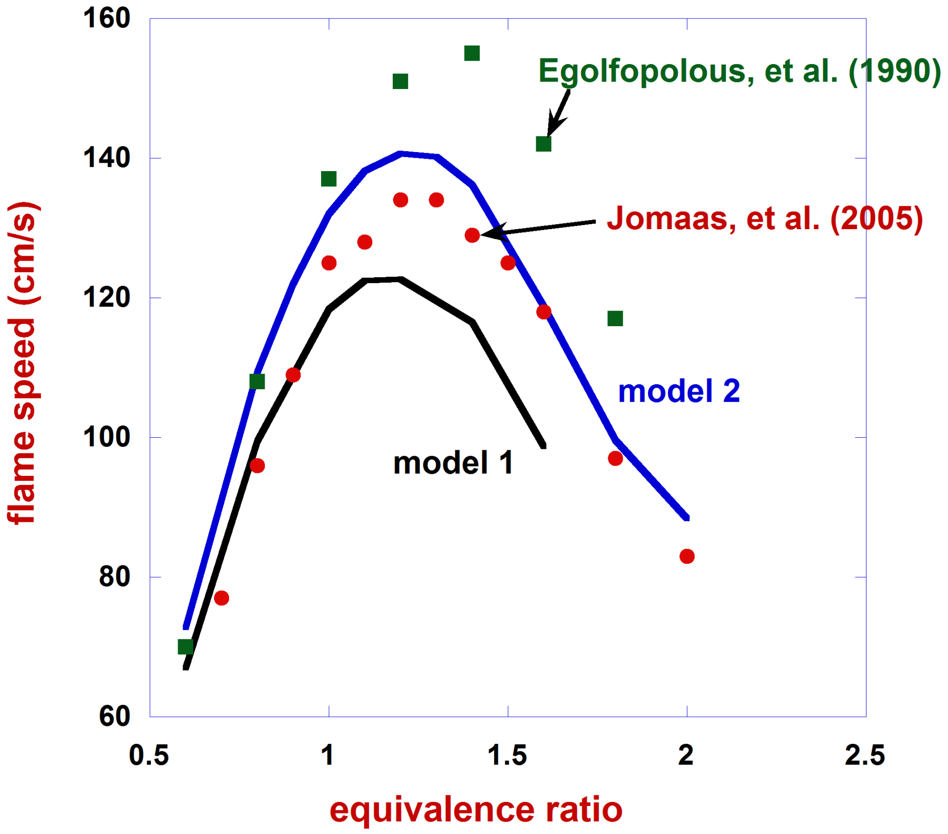
W. Duo, K. DamJohansen, K. Ostergaard, Can. J. Chem. Eng. 70 (1992) 1014-1020.



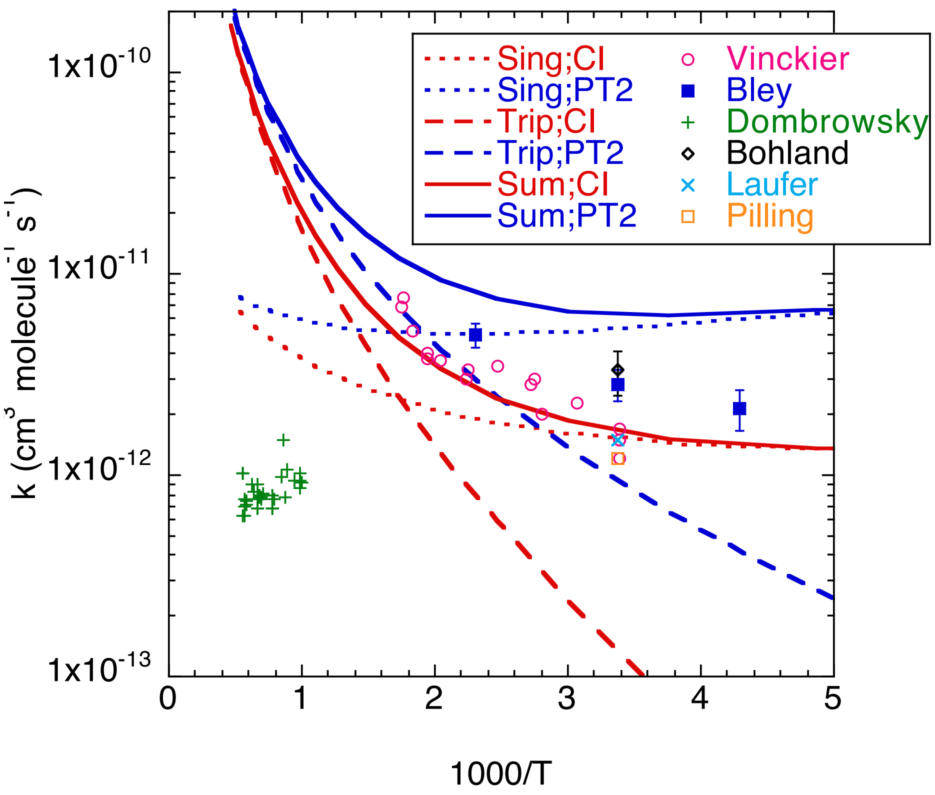
Mechanism Development C0-C3 Core Mechanism

Large scale update of Miller mechanism
Include Pressure Dependent Rate Coefficients

c2h2 flame speeds



$^3CH_2 + O_2$



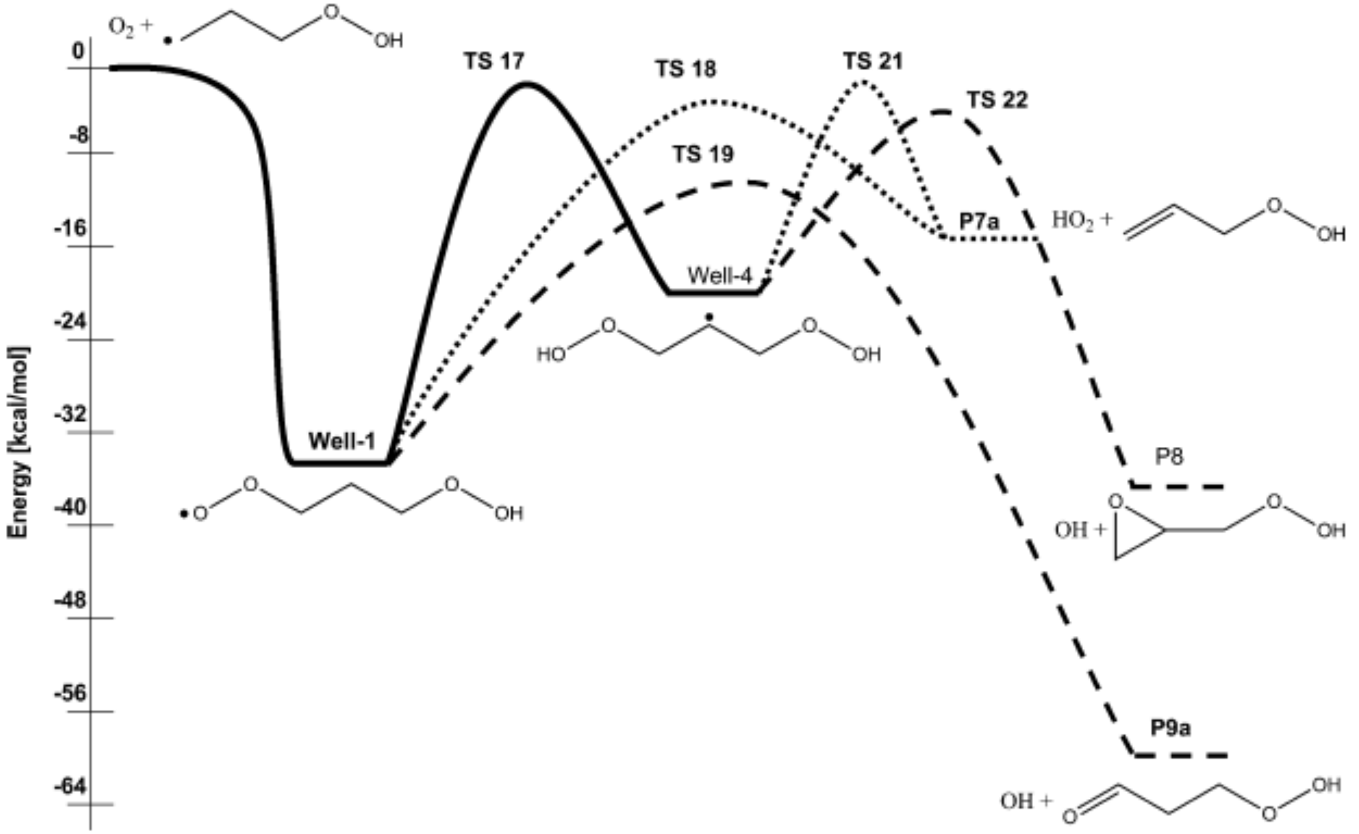
Miller, Klippenstein, and Glarborg, work in progress

Pressure Dependent Reactions $QOOH + O_2$

Modeling indicates $QOOH + O_2$ Central to Low Temperature Chain Branching but essentially no Elementary Kinetics Studies

$C_3H_6OOH + O_2$ Smallest Prototype

Goldsmith, Green, Klippenstein, J. Phys. Chem. A, 116, 3325 (2012)


O_2 +
OH
0
-8
-16
-24
-32
-40
-48
-56
-64
Energy [kcal/mol]
TS 17
TS 18
TS 21
TS 22
TS 19
P7a
HO_2 +
OH
Well-4
HO
OH
Well-1
O
OH
P8
OH +
O
OH
P9a
OH +
O
OH

Butanol Chemistry

CEFRC Developing Mechanism for Butanol Combustion

Sensitivity Analyses Suggest Need for Further Study of a Few Key Reactions

C_4H_9OH Decomposition - Isobutanol

C. W. Zhou, S. J. Klippenstein, J. M. Simmie, H. J. Curran, Proc. Comb. Inst. in press (2012); Paper 4D05

C_4H_9O Decomposition (α, β, γ, δ, and O radicals)

P. Zhang, C. K. Law, S. J. Klippenstein, (2012).

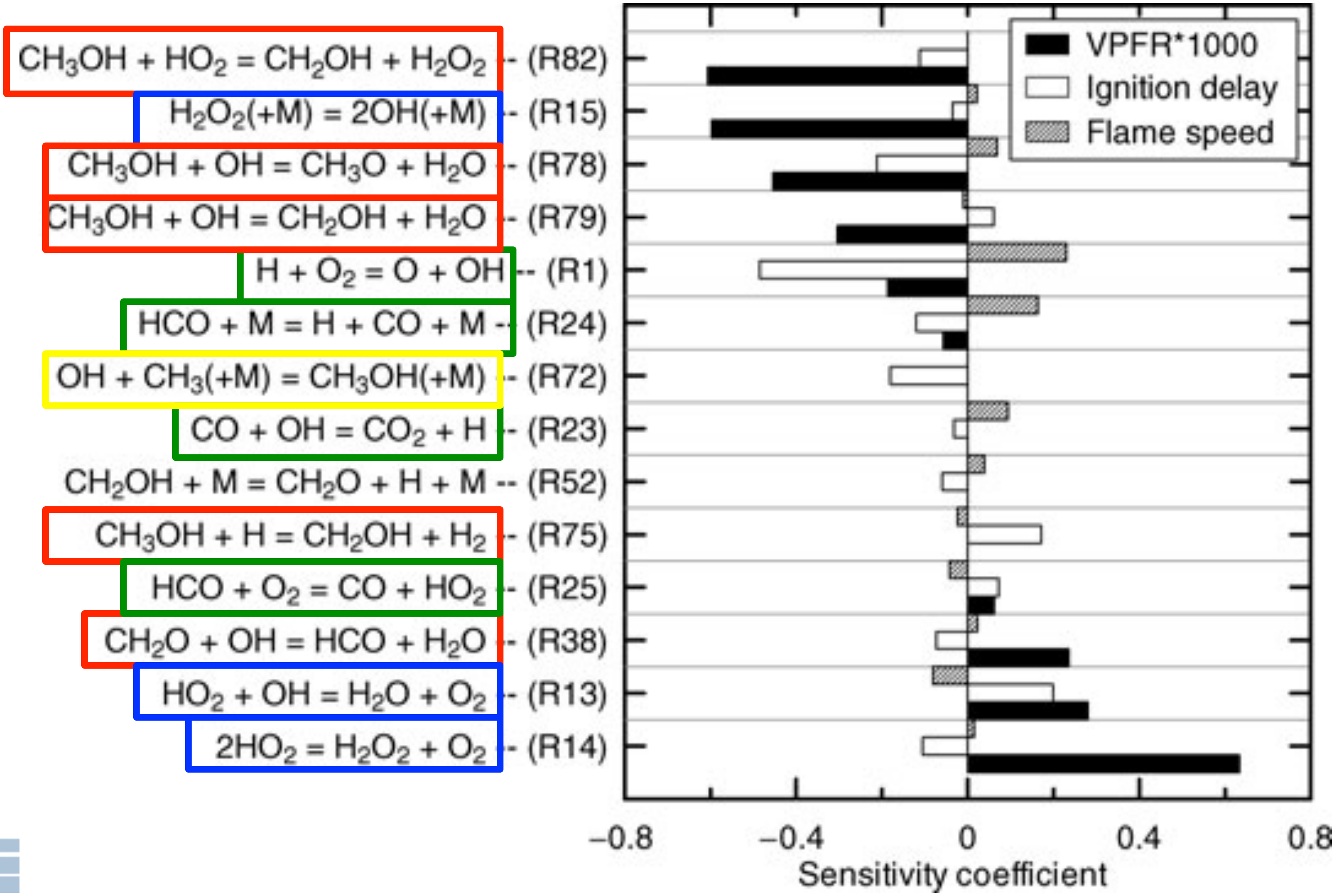
$C_4H_9O + O_2$ (α, β, γ, and δ radicals)

O. Welz, J. Zador, S. J. Klippenstein, in progress (2012).

Sensitivity for Methanol (CH_3OH) Combustion

Li, Zhao, Kazakov, Chaos, Dryer, Scire, IJCK, 39, 109 (2007)

Validated Against Ignition Delays, Flame Speeds, Species Profiles



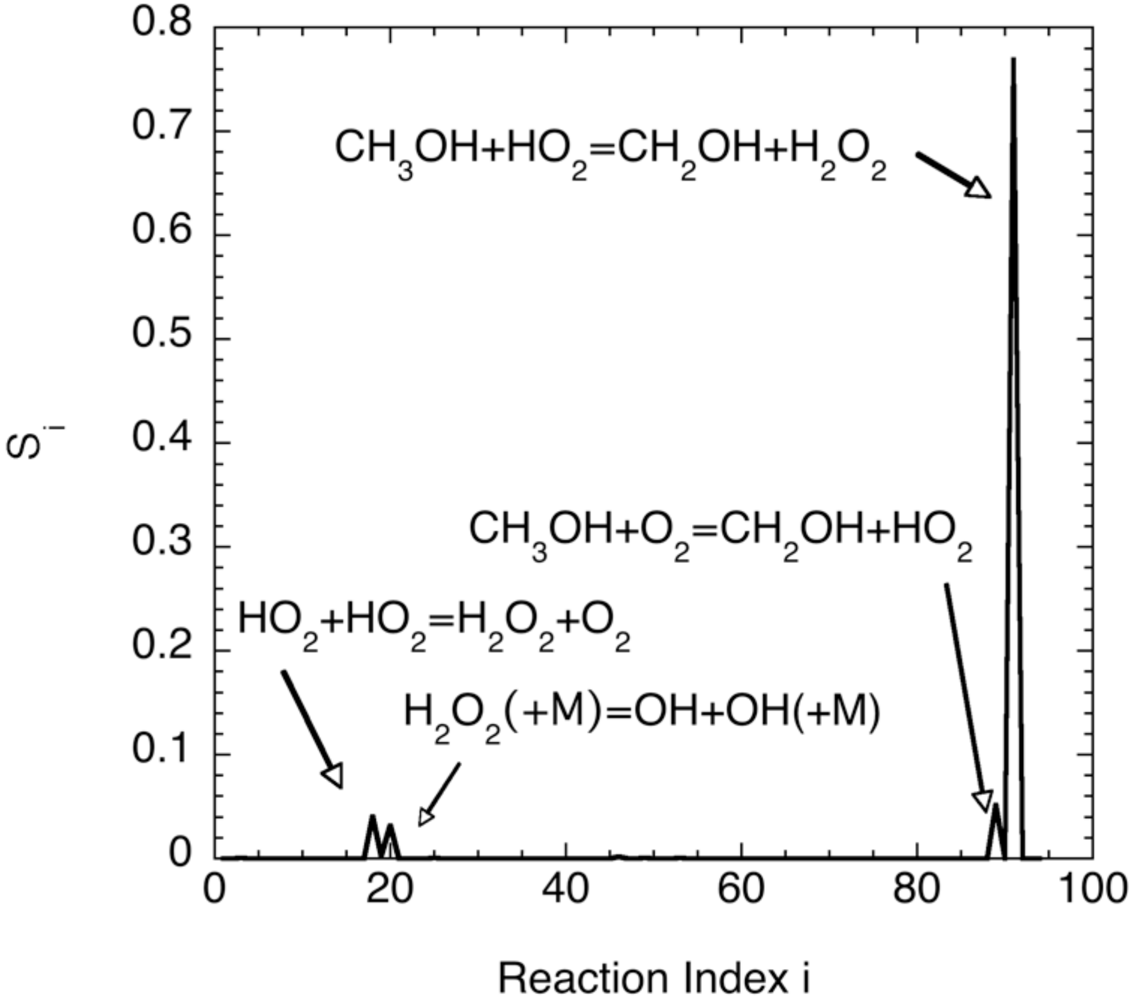
How to Improve for Engine Conditions - High Pressures/Non-Dilute?

Global uncertainty analysis

- Indicates reaction with dominant contribution to overall uncertainty
- Theoretical predictions of selected rate coefficients
- How accurate?

Klippenstein, Harding, Davis, Tomlin, Skodje Proc. Comb. Inst. 33, 351 (2011).

Variance Analysis for the Ignition Delay



Transition State Theory

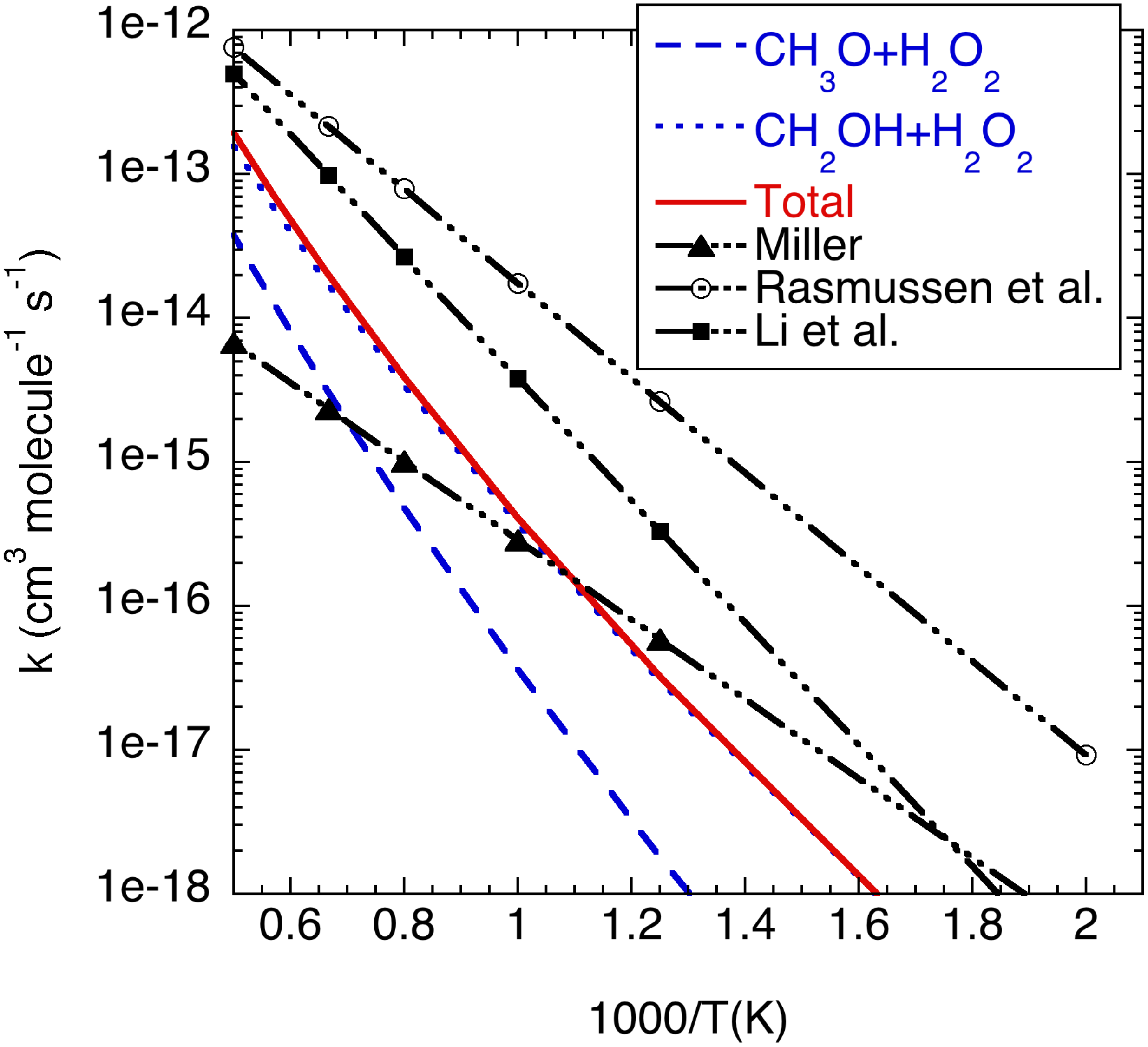
Complete torsional sampling to find torsional minima

Torsional modes treated as uncoupled 1-dimensional hindered rotors

Asymmetric Eckart Tunneling

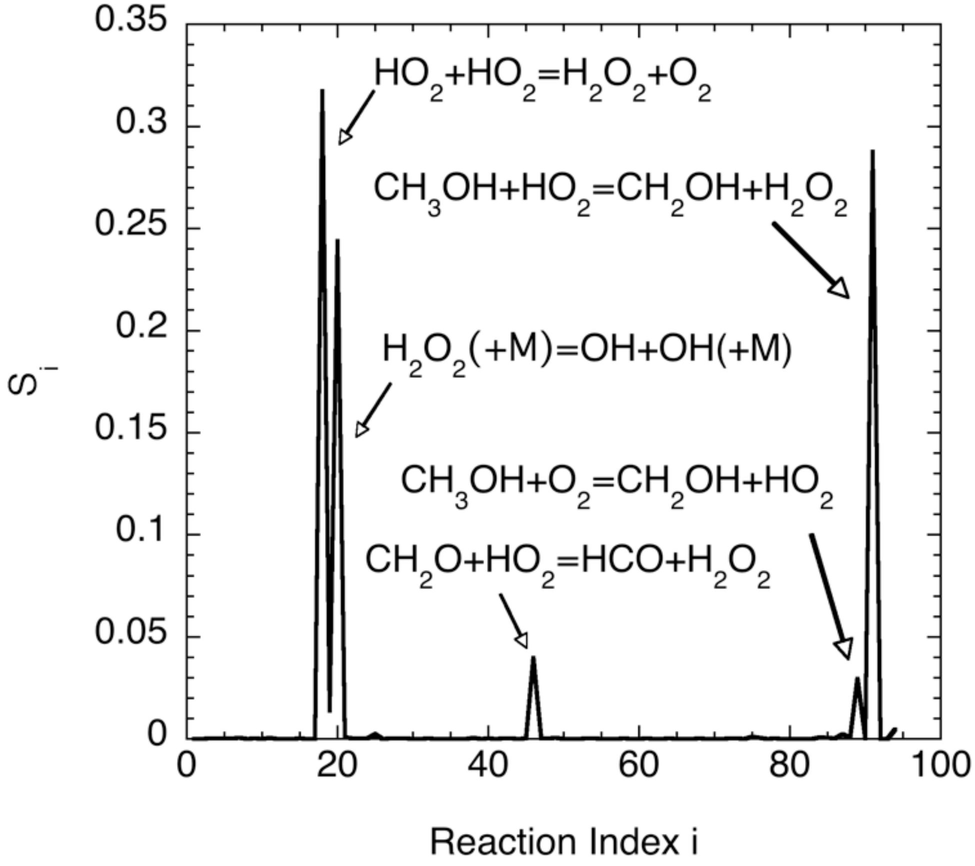
Other modes – harmonic oscillators and rigid rotors

$CH_3OH + HO_2$

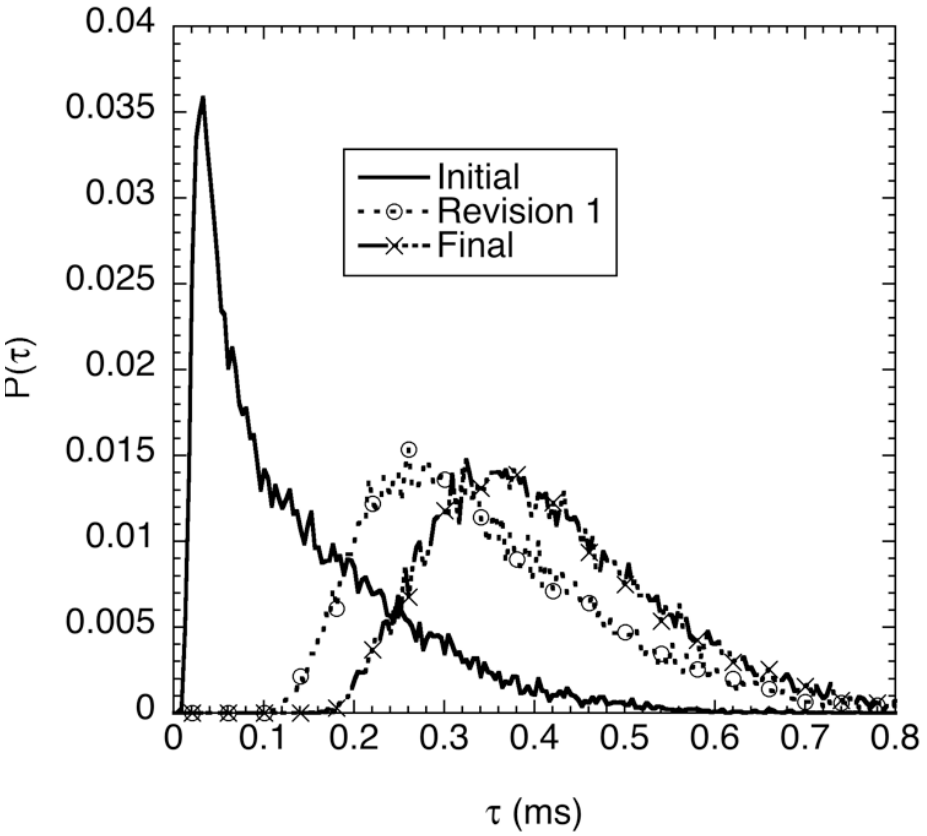


Change in ignition characteristics

Final Uncertainty Analysis



Predicted Ignition Delays

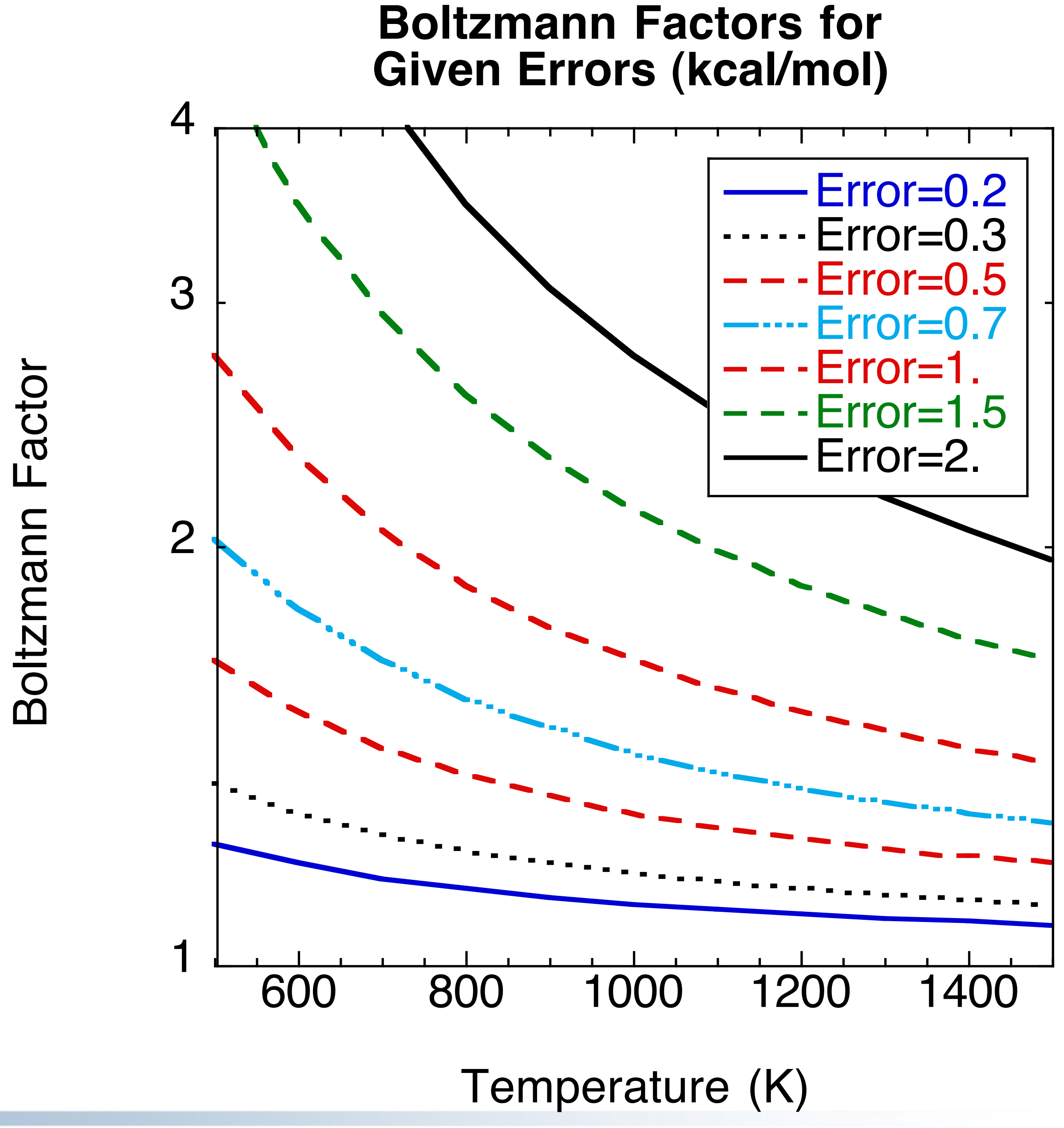


<τ>		Width/<τ>	
Initial	0.11	Initial	2.0
Final	0.40	Final	0.70

How Accurate are our Predictions?

- Currently a Factor of 2-3 Uncertainty
- Compare with Experiments
  - Experience from many comparisons
- Analysis of uncertainty for underlying factors in theoretical analysis
  - Barrier Height Uncertainties
  - Vibrational Frequency Uncertainties
  - Anharmonicity Corrections
- Do Mechanisms Improve?
- Trying to reduce uncertainties to about 1.2-1.3

Reactions with Barriers



Combustion Thermochemistry Database

HEAT (Stanton and coworkers); Wn (Martin and coworkers); Focal Point (Allen and coworkers)

CCSD(T)/TZ optimizations and Frequencies

CCSD(T)/CBS from CCSD(T)/AQZ',A5Z'

CCSDT(Q)/DZ

Core-Valence CCSD(T)/CBS; TZ and QZ

Relativistic from DKH with CI/TZ

DBOC from HF/cc-pVTZ

Anharmonic corrections from B3LYP/6-311++G**

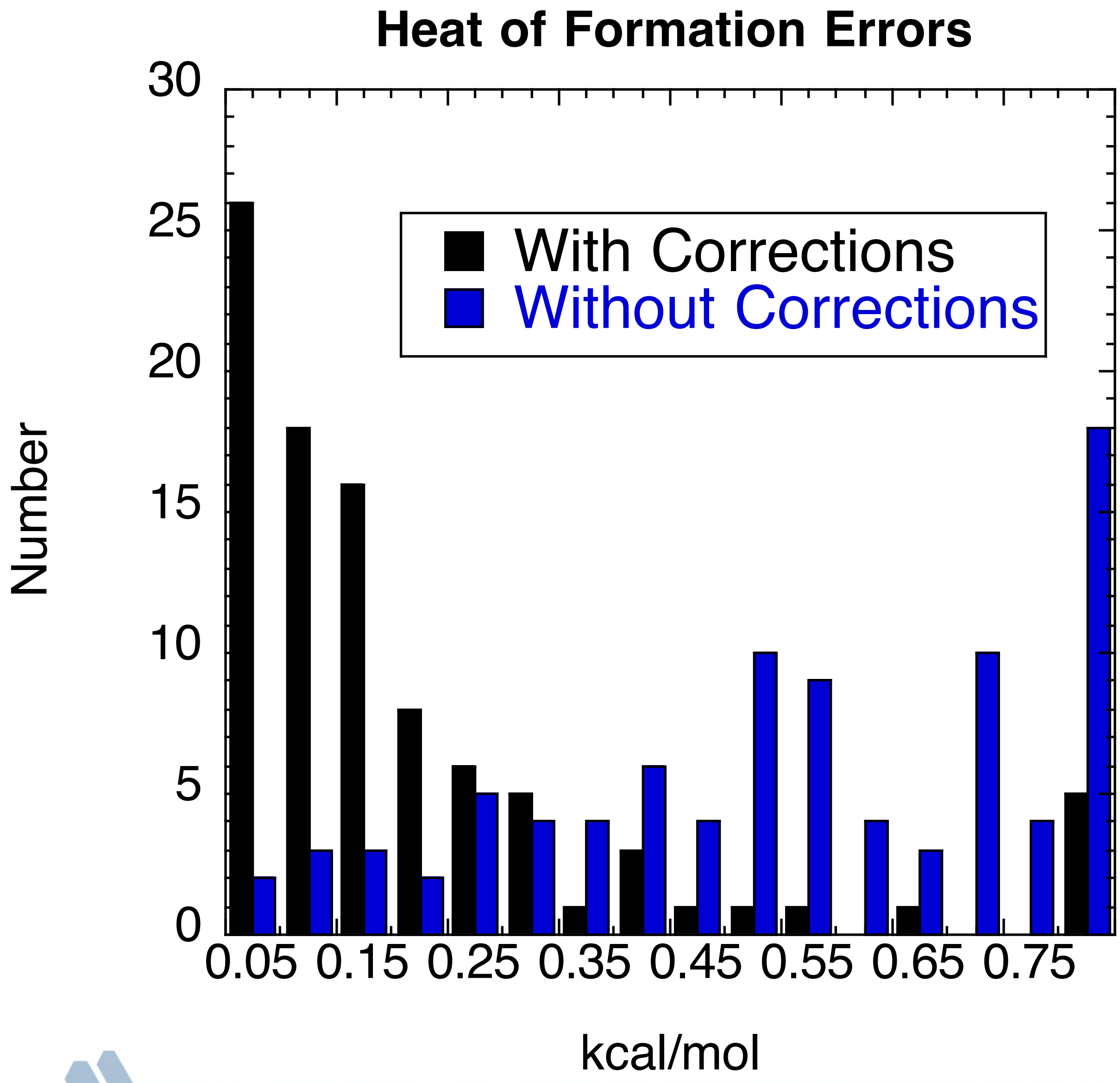
Heats of formation relative to H_2, CH_4, H_2O, NH_3

5 Heavy Atoms

Size of Individual Corrections

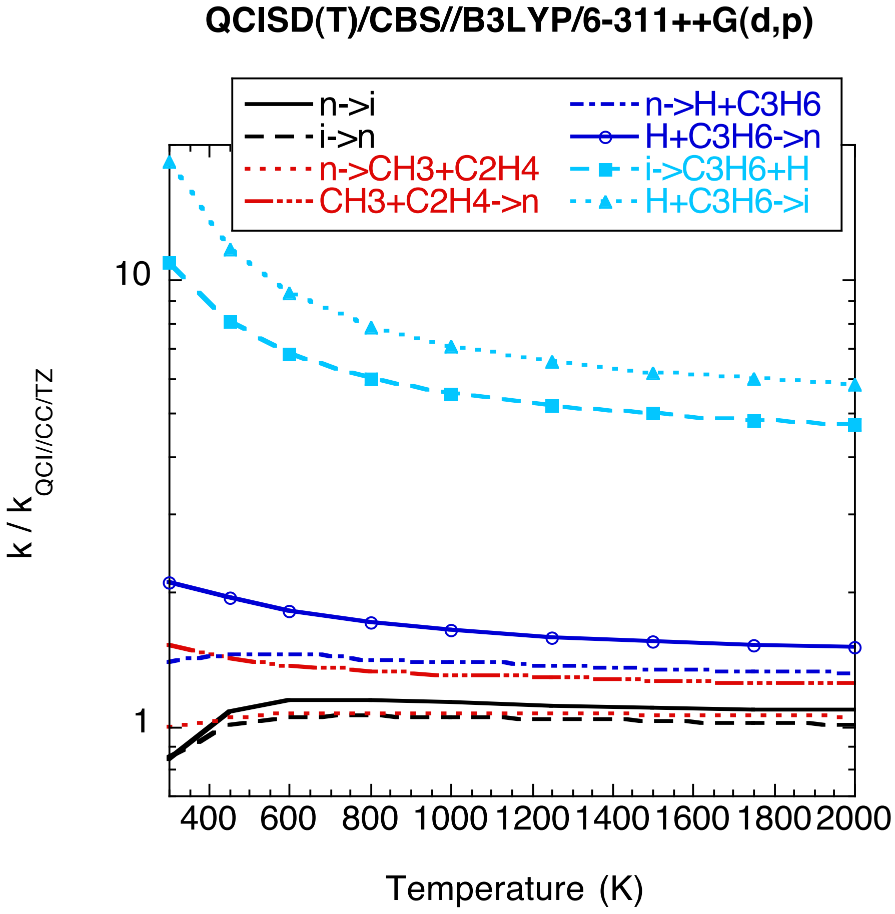
	Mean	MAD	RMSD	Variance
CCSDT(Q)	-0.36	0.42	0.62	0.46
Core-Valence	0.54	0.54	0.60	0.28
Anharmonicity	0.47	0.49	0.59	0.32
Relativistic	-0.16	0.16	0.20	0.11
DBOC	0.10	0.11	0.14	0.09

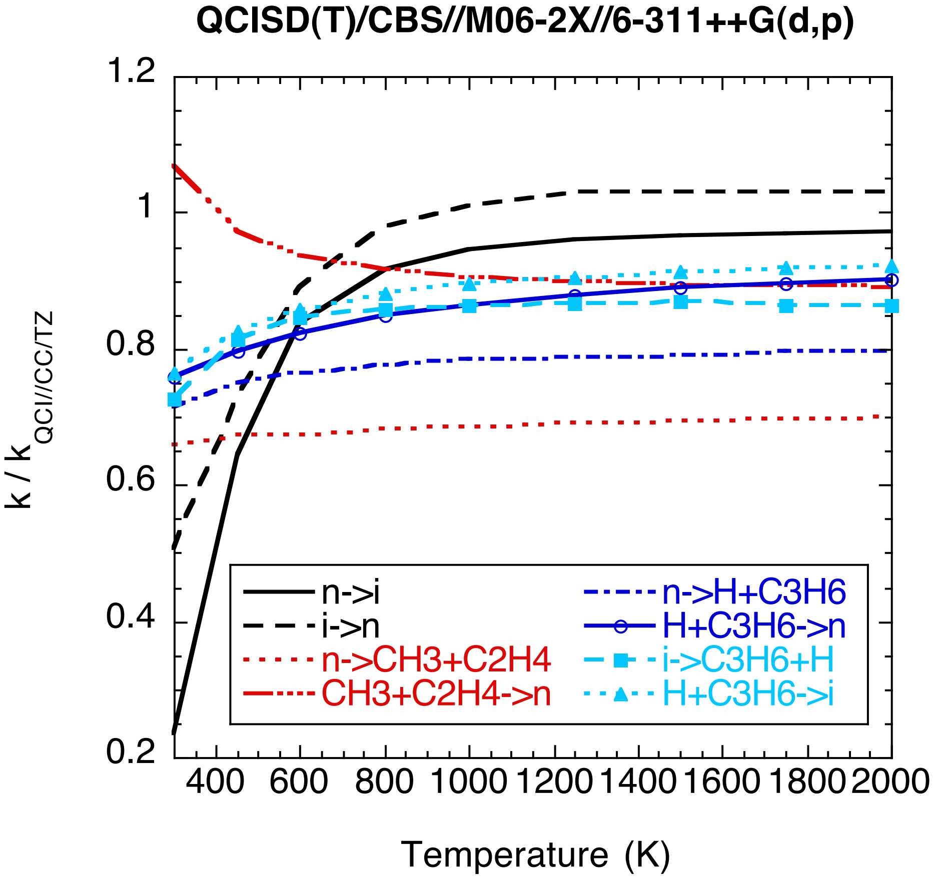
Accuracy vs ATcT from Ruscic



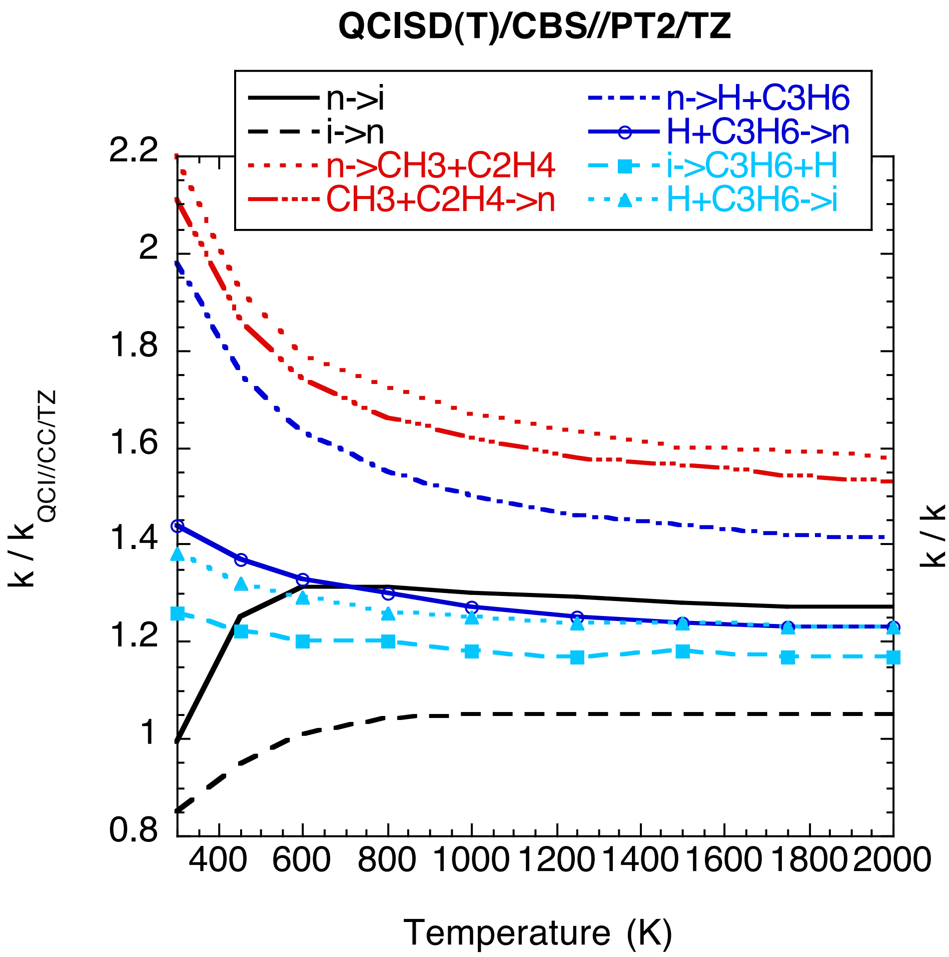
H, O, OH, O2, HO2, H2O2, O3, C, CH, CH2, 1CH2, CH3, CO, HCO, COH, CH2O, HCOH, CH2OH, CH3O, CO2, HOCO, HCO2, OCHOH, CH3O2, CH3OOH, C2, C2H2, H2CC, C2H3, CCH3, C2H4, CHCH3, C2H5, C2H6, CCO, 1CCO, HCCO, CH2CO, HCCOH, CH3CO, CH3CHO, CH2CHOH, CH3CHOH, C2H4OH, CH3CH2O, C2H5OH, CH3OCH3, OCHCHO, CH3C(O)OH, CH2CCH, CH3CCH, CH2CCH2, -CH2CHCH-, CH3CHCH2, CH3CH2CH3, N, NNH, NHNH, H2NN, NHNH2, NH2NH2, NO, HNO, NOH, H2NO, HNOH, H2NOH, N2O, NO2, NO3, CN, HCN, CNH, H2CN, HCNH, CH3N, CH2NH, CH3NH, CH2NH2, CH3NH2, NCO, HNCO, HCNO, NCOH

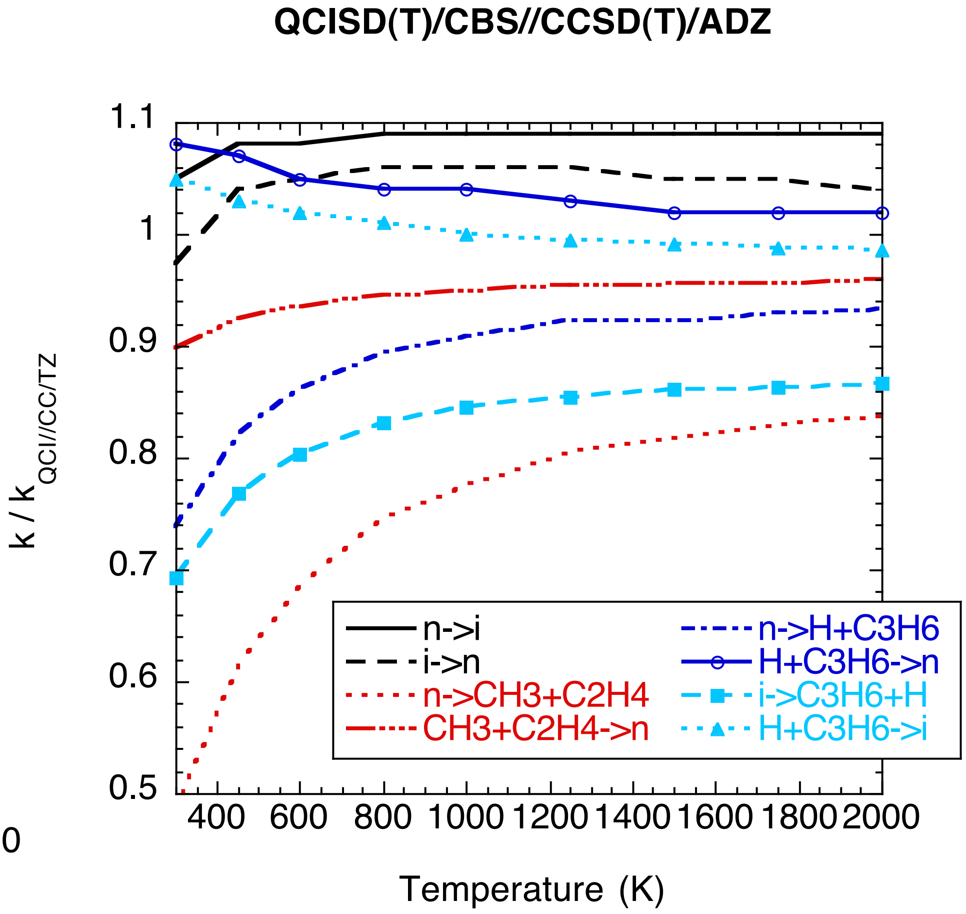
Rovibrational Properties Reactions on C_3H_7 PES





Rovibrational Properties





Coupling of Uncertainties

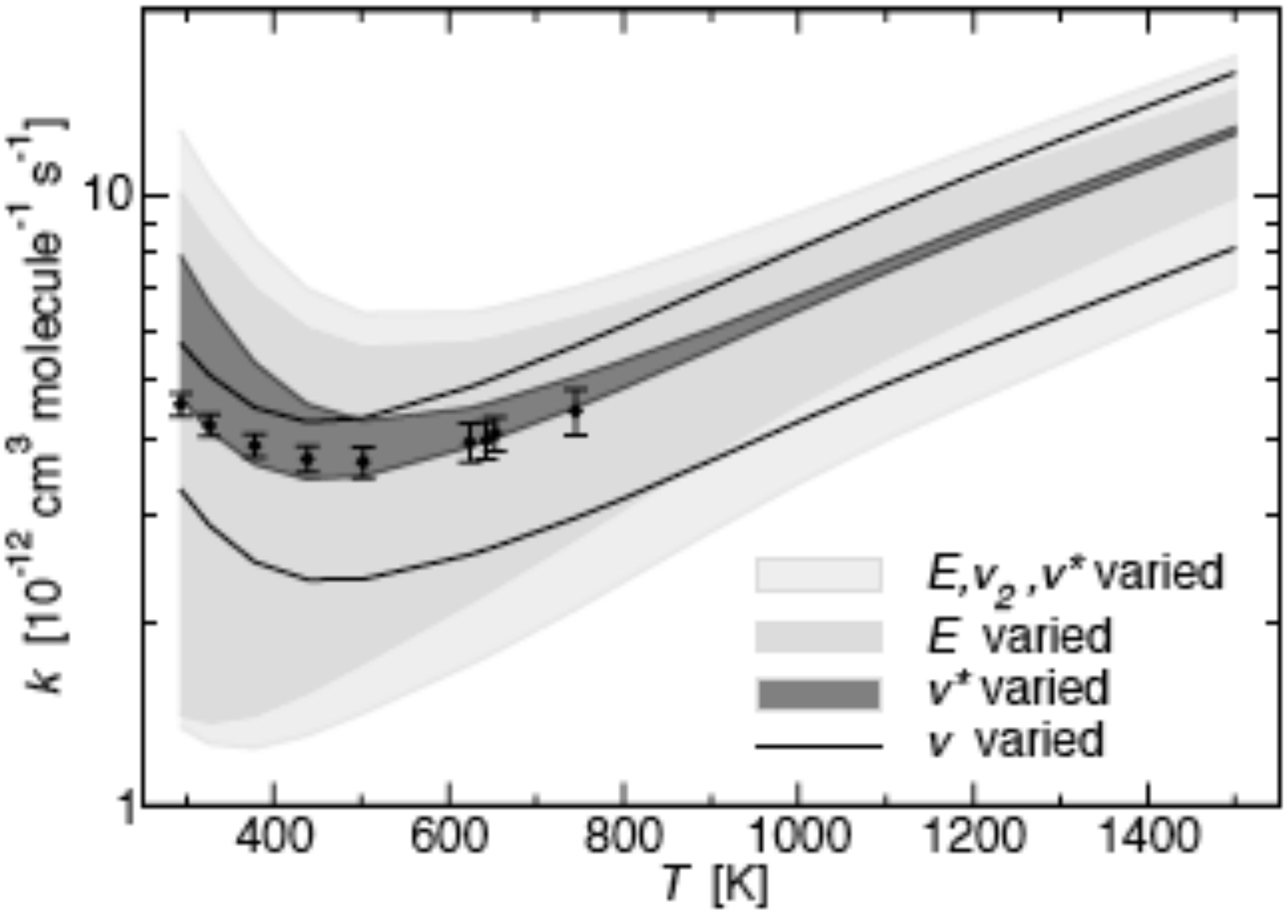
$\Delta E = \pm 1.0$ kcal/mol

$\Delta v = 1.5$ factor

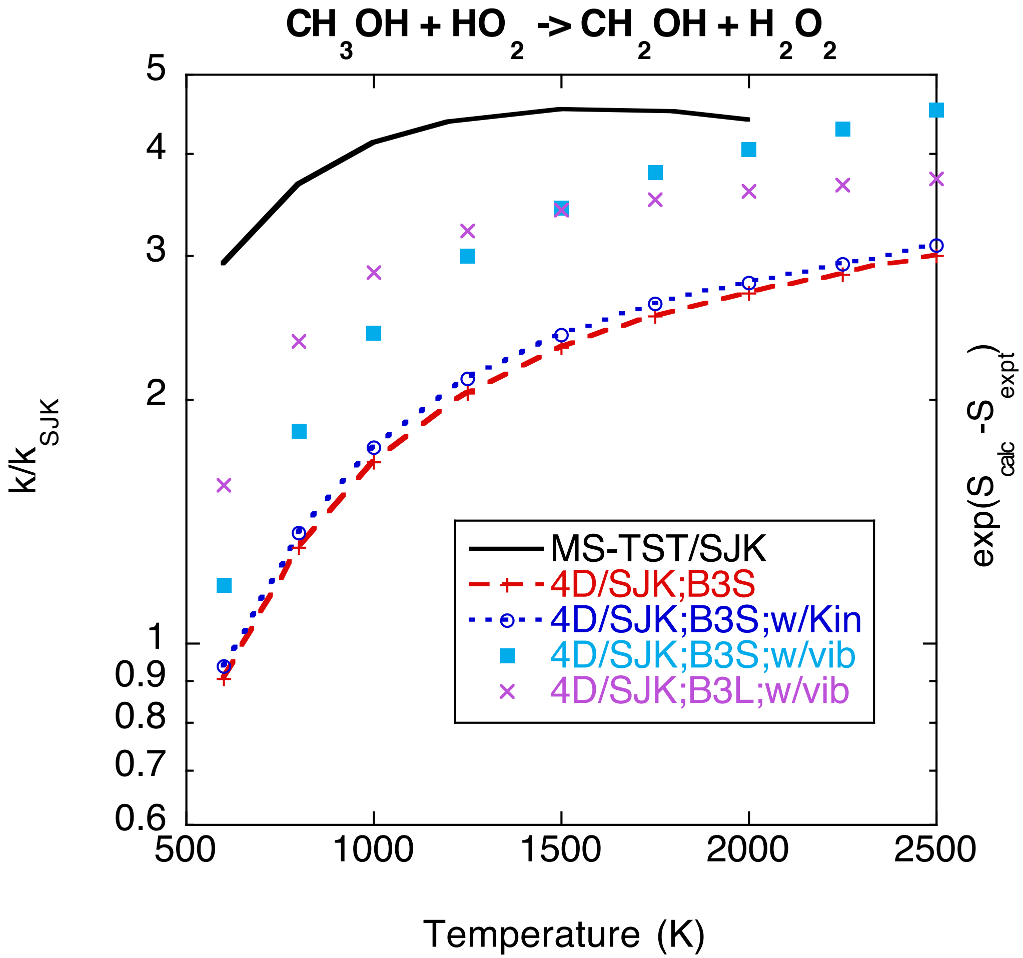
$v^{\neq} = (50,850)$ cm^{-1}

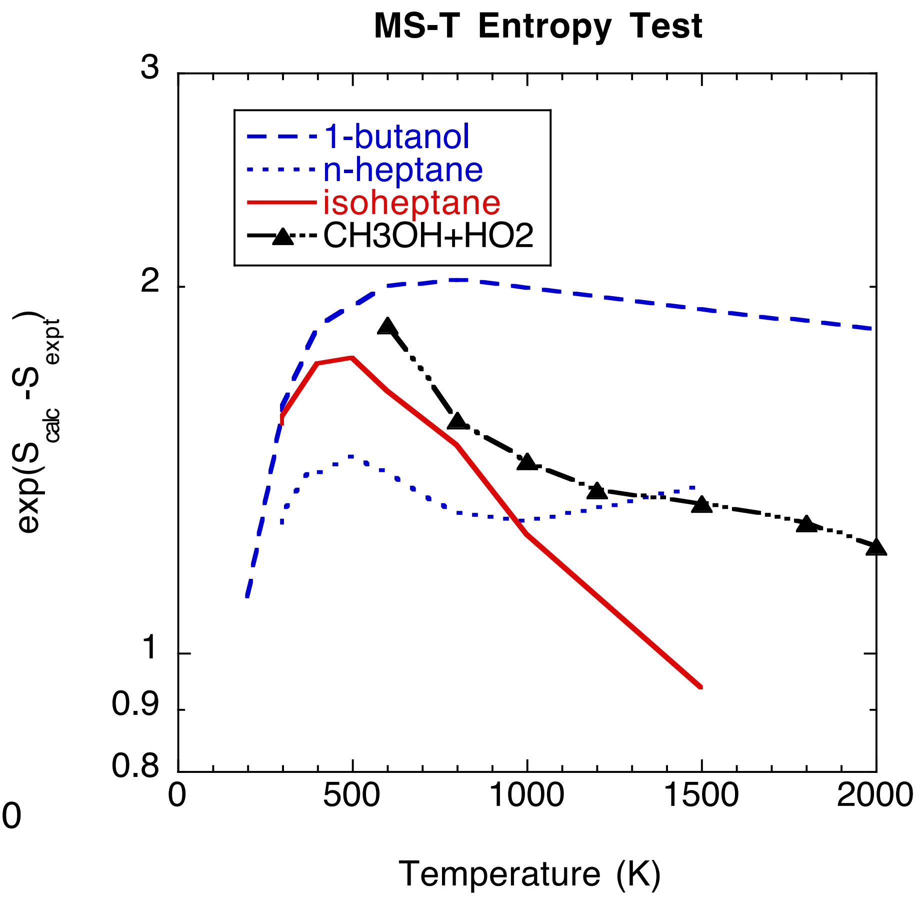
J. Prager, H. N. Najm, J. Zador
Proc. Comb. Inst.
In press (2012)
Paper 5D03

$CH_3CH(OH)CH_3 + OH \rightarrow CH_3C^{\bullet}(OH)CH_3 + H_2O$



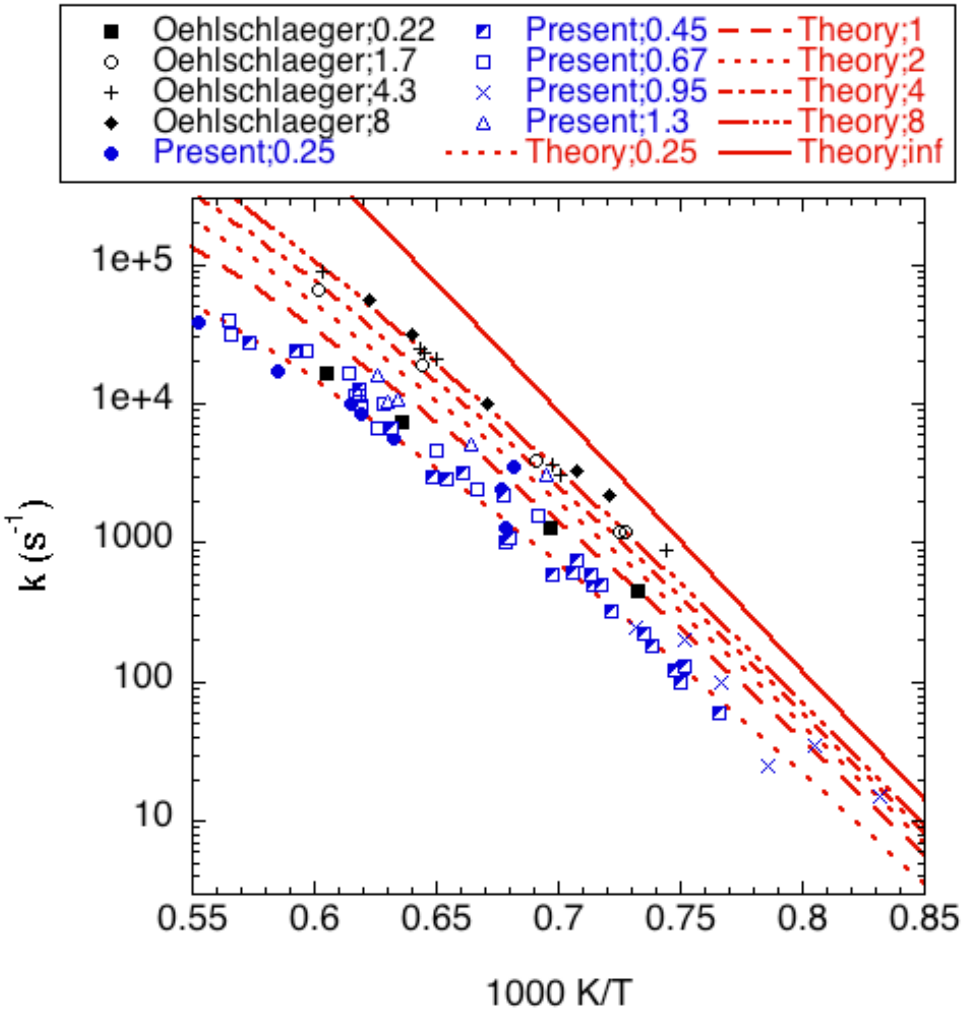
Direct Sampling of Torsions





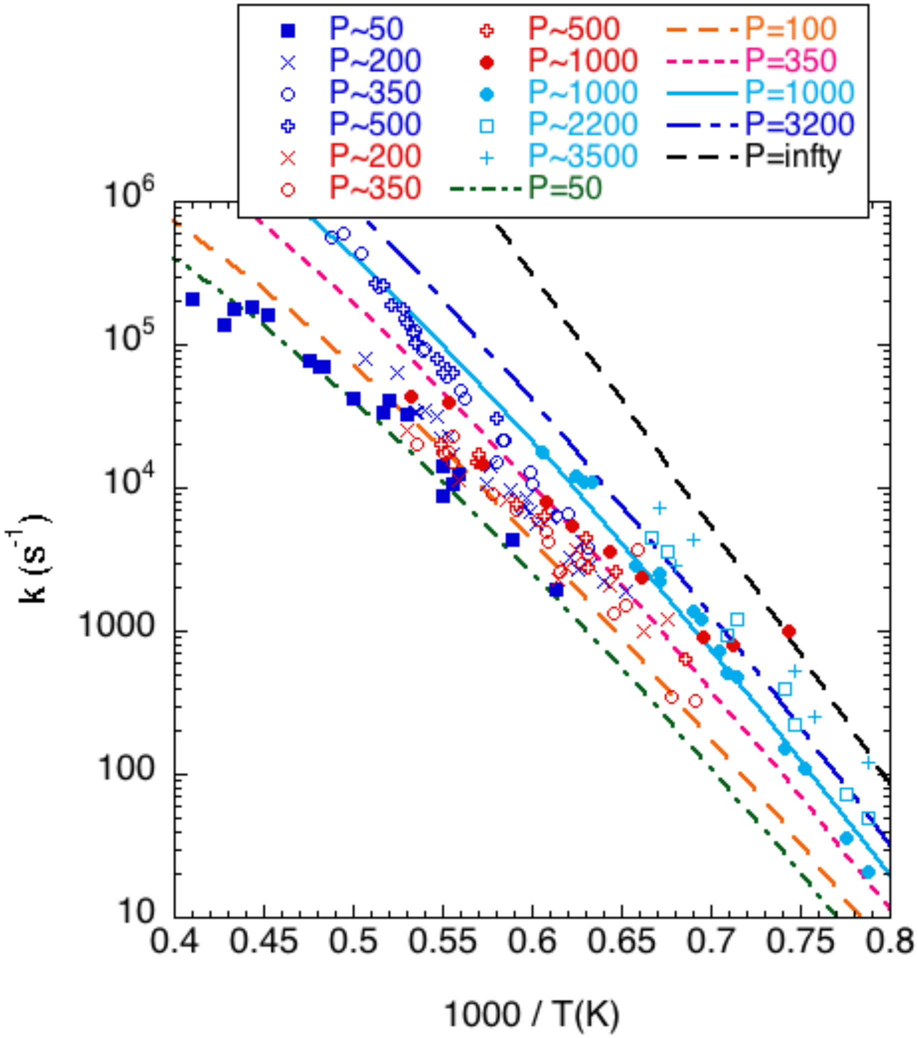
Pressure Dependence: Comparison with Expt

Propane Decomposition



$\langle \Delta E_{down} \rangle = 100\ (T/300)^{0.85}\ \mathrm{cm}^{-1}$

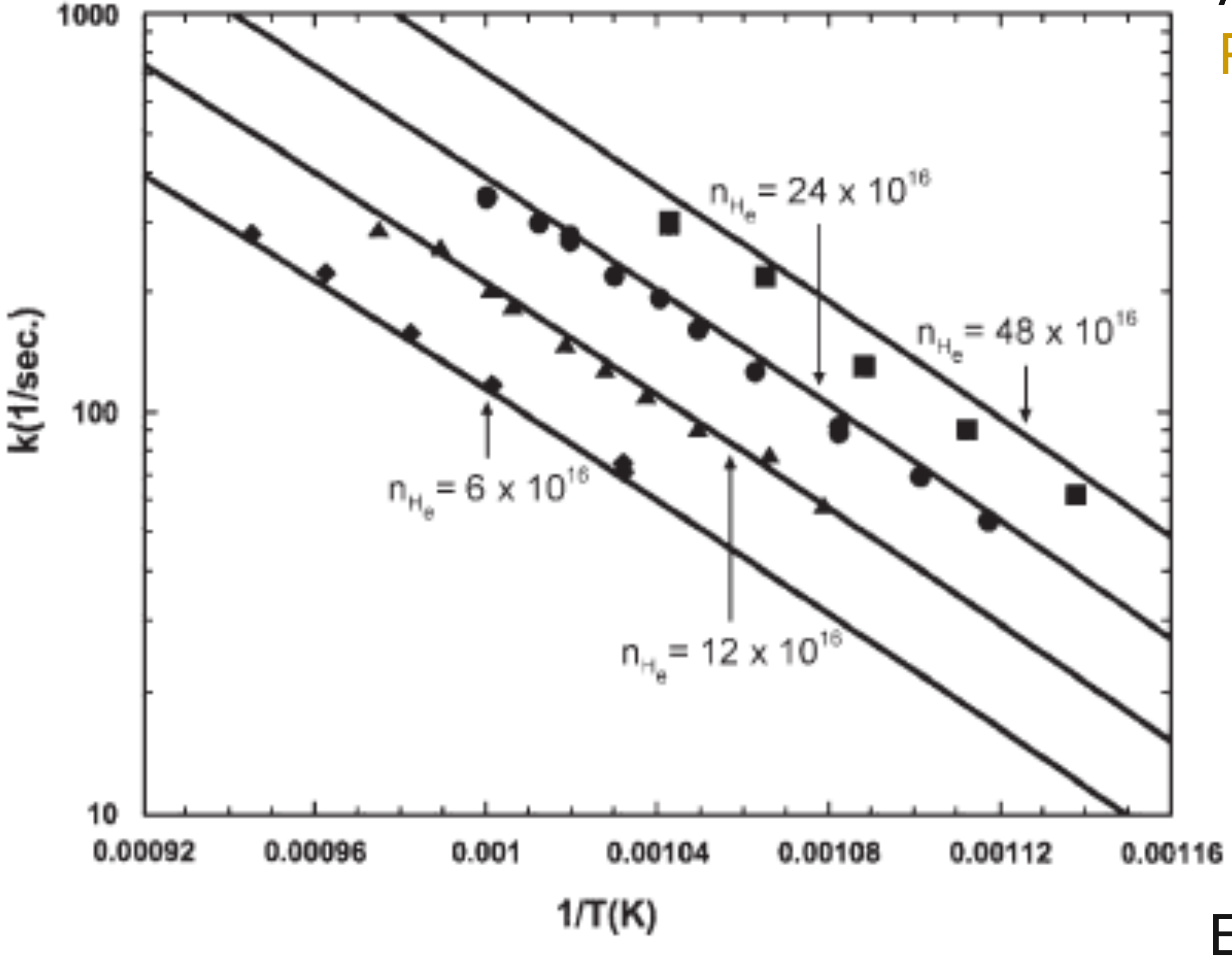
Acetaldehyde Decomposition



$\langle \Delta E_{down} \rangle = 150\ (T/300)^{0.85}\ \mathrm{cm}^{-1}$

C_2H_3 -> C_2H_2 + H

Energy Transfer
Jasper & Oana
AITSTME
Pelzer, Miller, SJK



Delta E_{down}

Fit
237 cm^{-1}

Trajectory
470 cm^{-1}

Experiment
Knyazev & Slagle

A Priori Predictions of Pressure Dependence

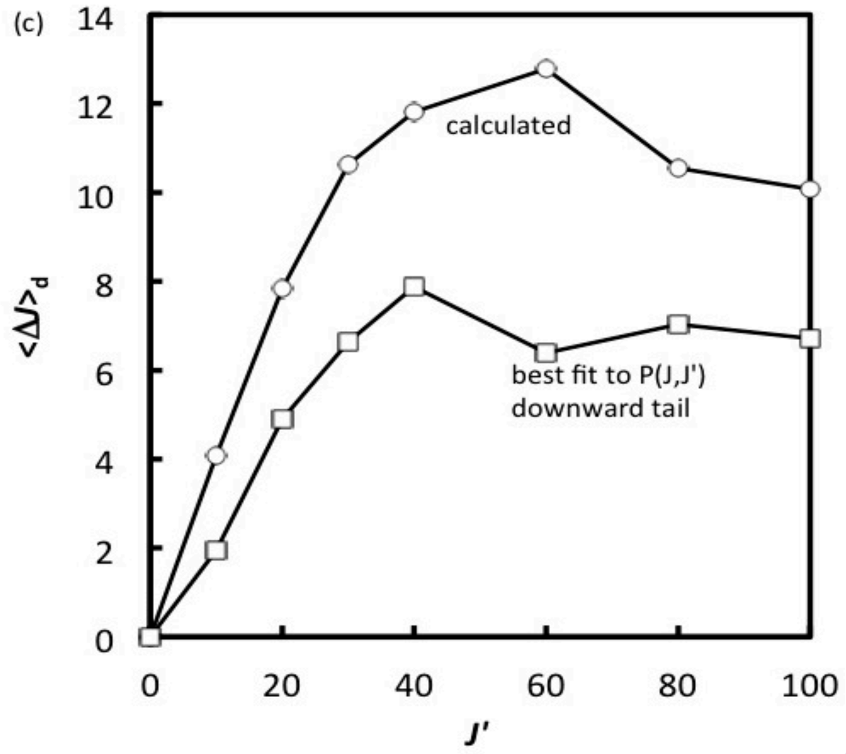
Trajectory Simulations of Energy Transfer

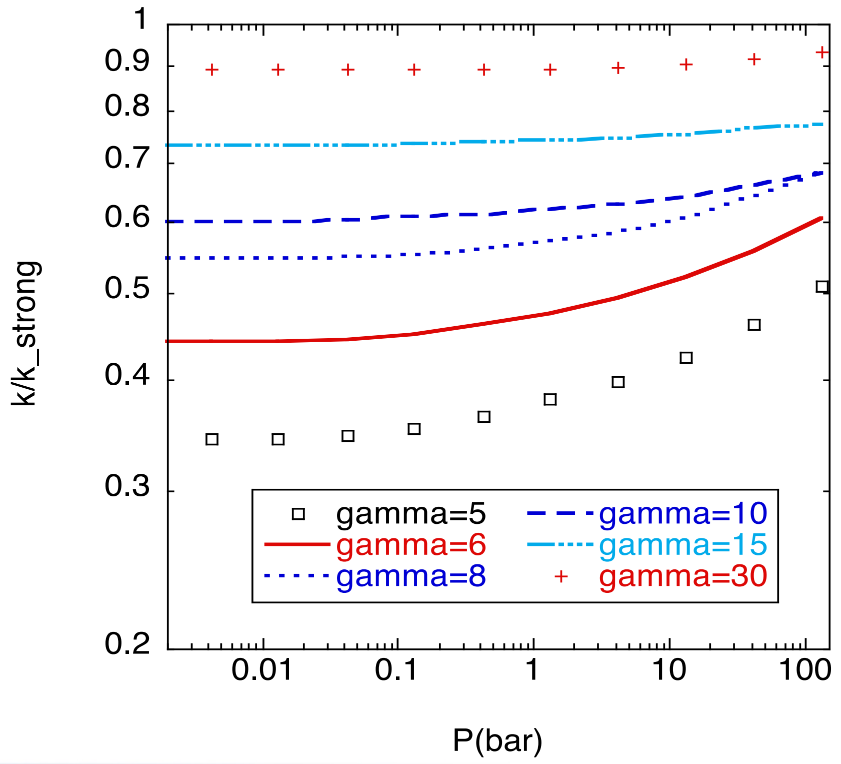
A Priori P(E’-> E)

1D Master Equation Assumes Strong Collider in J – Not Valid

P(E’,J’->E,J) ΔE_{down} ΔJ_{down}

2-Dimensional Master Equation (E,J)





Coupling of Uncertainties: n-propyl + O_2

O_2+n-C_3H_7 ⇌ RO_2 [R1]

⇌ QOOH-1 [R2]

⇌ HO_2+propene [R3]

⇌ OH+propene-oxide [R4]

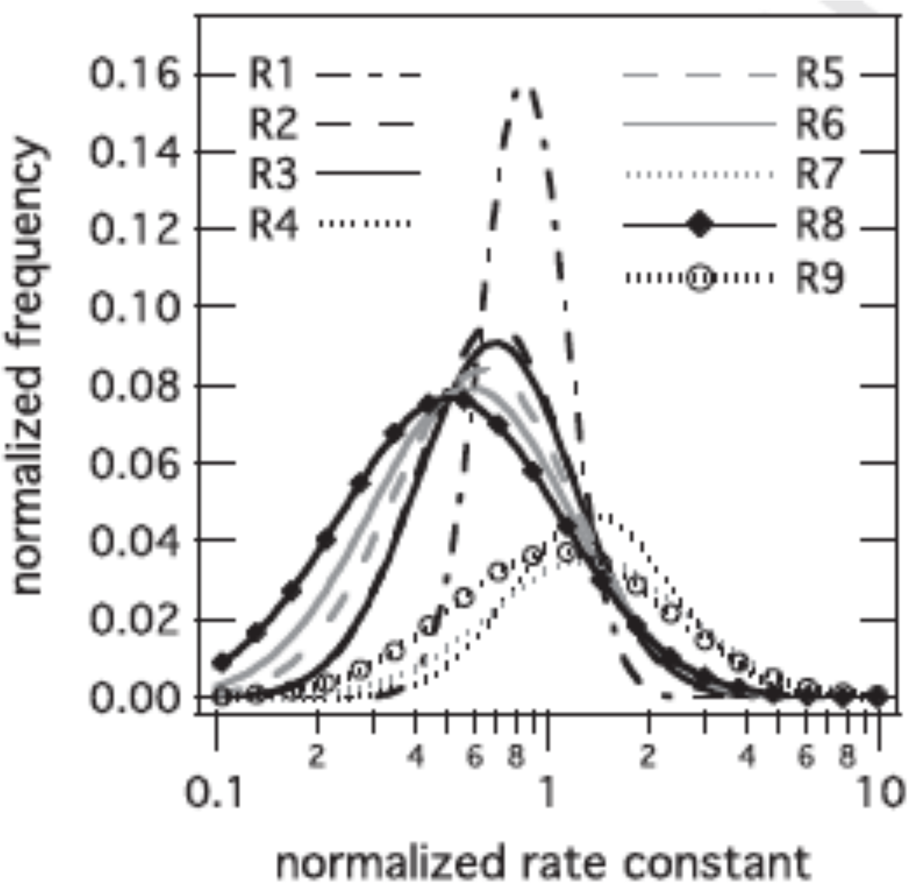
RO_2 ⇌ QOOH-1 [R5]

⇌ HO_2+propene [R6]

⇌ OH+propene-oxide [R7]

QOOH-1 ⇌ HO_2+propene [R8]

⇌ OH+propene-oxide [R9]

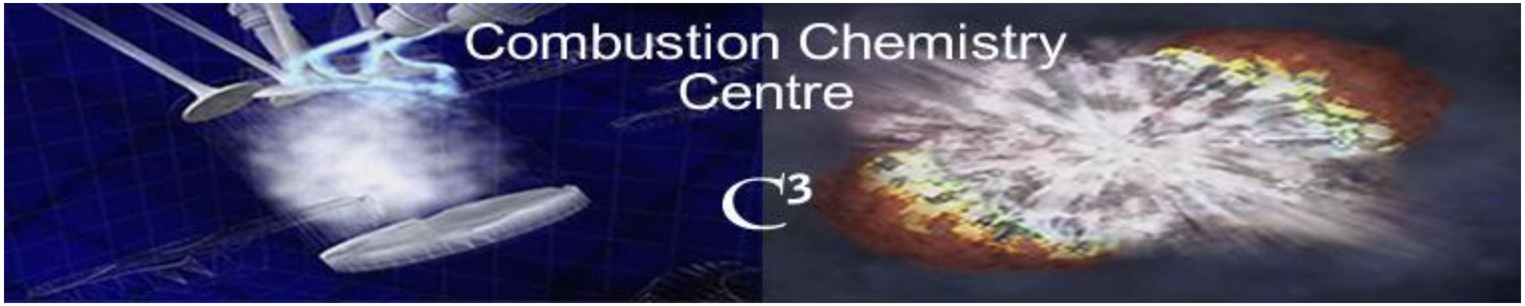


C. F. Goldsmith, A. S. Tomlin, S. J. Klippenstein, Proc. Comb. Inst. 34, in press (2012) Paper 2D09

Funding

US-Department Of Energy

1. Chemical-Physics Program – Chemical Dynamics in the Gas Phase
2. Argonne-Sandia Consortium on High Pressure Combustion Chemistry
3. Combustion Energy Frontier Research Center
4. An Expert Ab Initio Transition-State-Theory-Based Master Equation Code


Combustion Chemistry
Centre
C3

Kinetic Mechanism Development for Hydrocarbons and Oxygenated Fuels

Dr. Henry Curran and Dr. Philippe Dagaut

Combustion Chemistry Centre, NUI Galway, Ireland

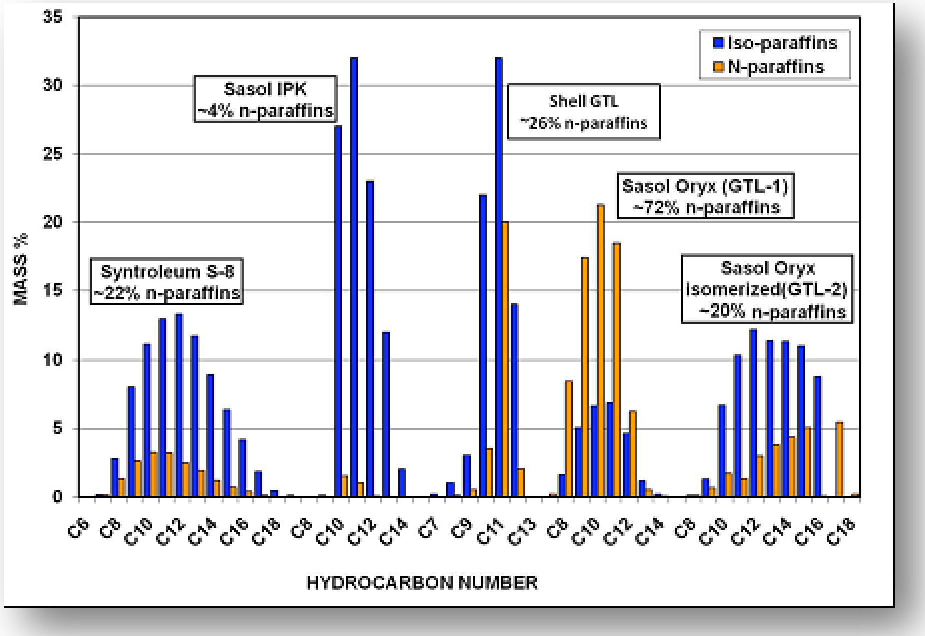
CNRS Orleans, France

Lecture
1st Workshop on Flame Chemistry
July 28th, 2012

NUI Galway
OÉ Gaillimh

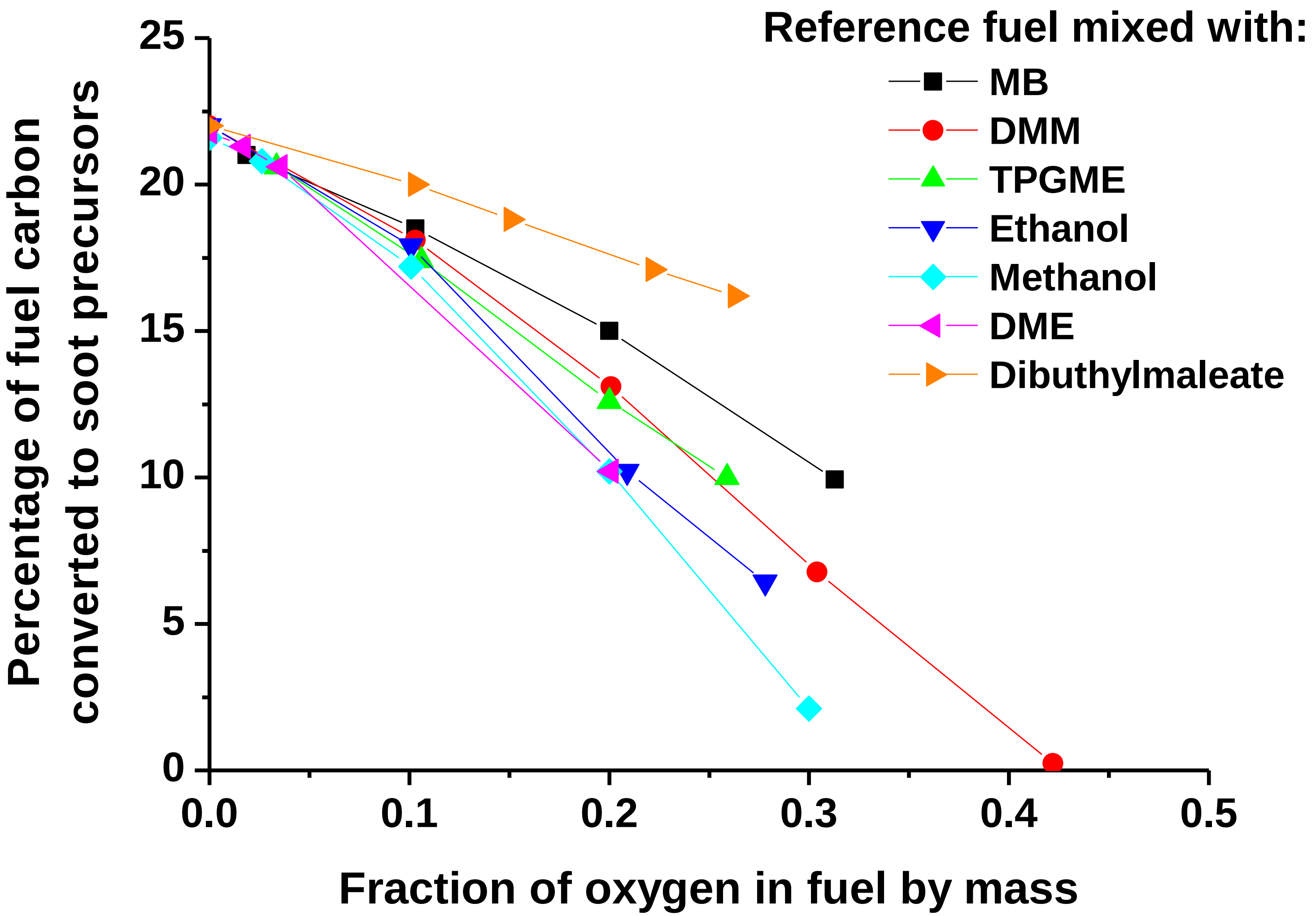
Future HC fuels - many sources

- Some petroleum will still be available
- Oil sands, oil shale
- Coal-to-liquids
- Fischer – Tropsch
- Natural gas
- Hydrogen
- Bio-derived fuels
  - Ethanol, butanol, algae
  - Biodiesel from vegetable and animal oils



- Chemical kinetics to understand and simulate
  - complex behaviour (ignition, NTC, cool flames…)
    - reactivity (extent of conversion, heat release)
      - product / pollutant formation

How well an oxygenated fuel works depends on its molecular structure

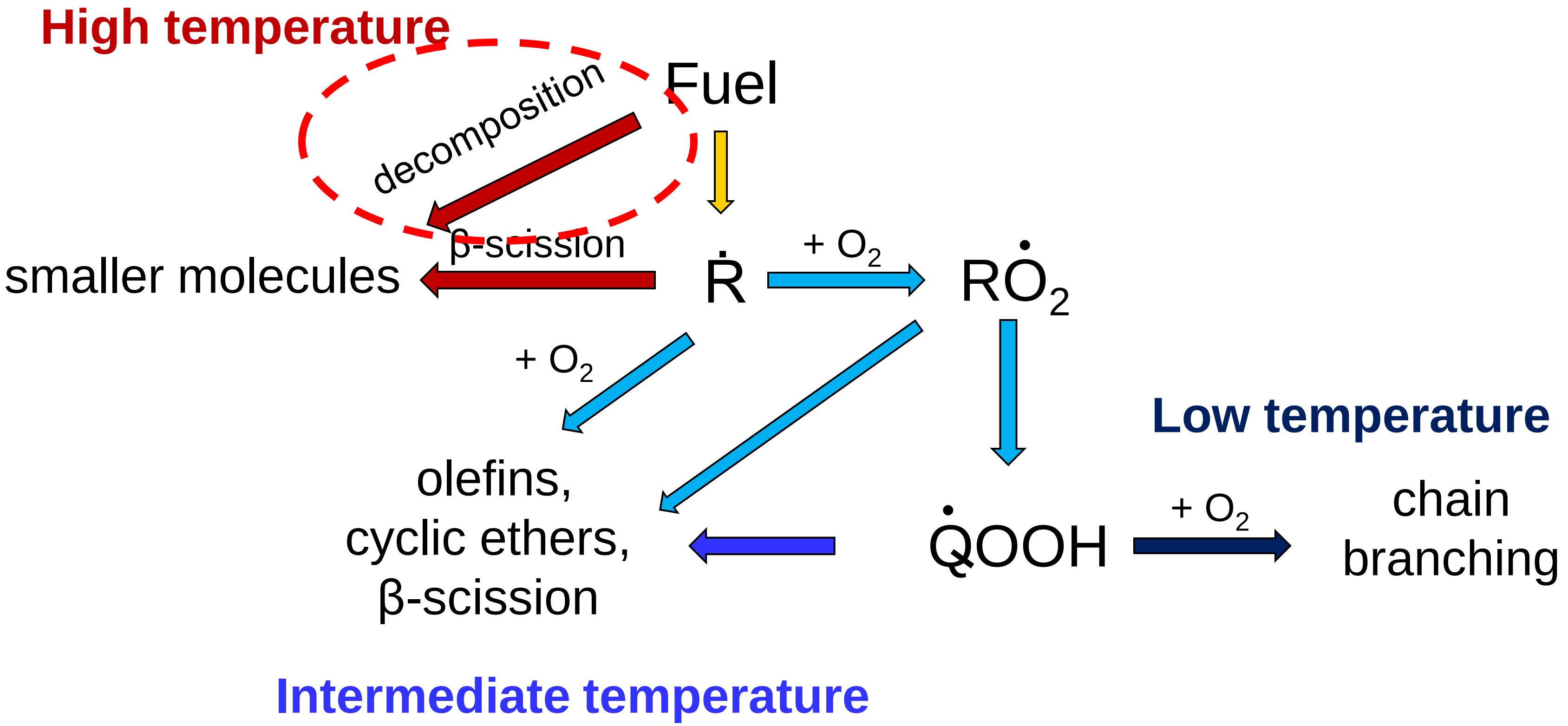


Miyamoto *et al.* Paper No. SAE 980506 (1998).
Westbrook *et al.* J. Phys. Chem. A (2006) *110:* 6912–6922.

Oxygenated fuels

- Alcohols (methanol, ethanol, propanol, butanol)
- Ethers (DME, DEE, EME, MTBE, ETBE)
- Esters (methyl and ethyl esters)
- Ketones (acetone, EMK, DEK)
- Furans (methyl furan, di-methyl furan)

General reaction scheme



High temperature

Fuel

decomposition

β-scission

smaller molecules

$\dot{R}$

+ O_2

$R\dot{O}_2$

+ O_2

Low temperature

olefins,
cyclic ethers,
β-scission

$\dot{Q}OOH$

+ O_2

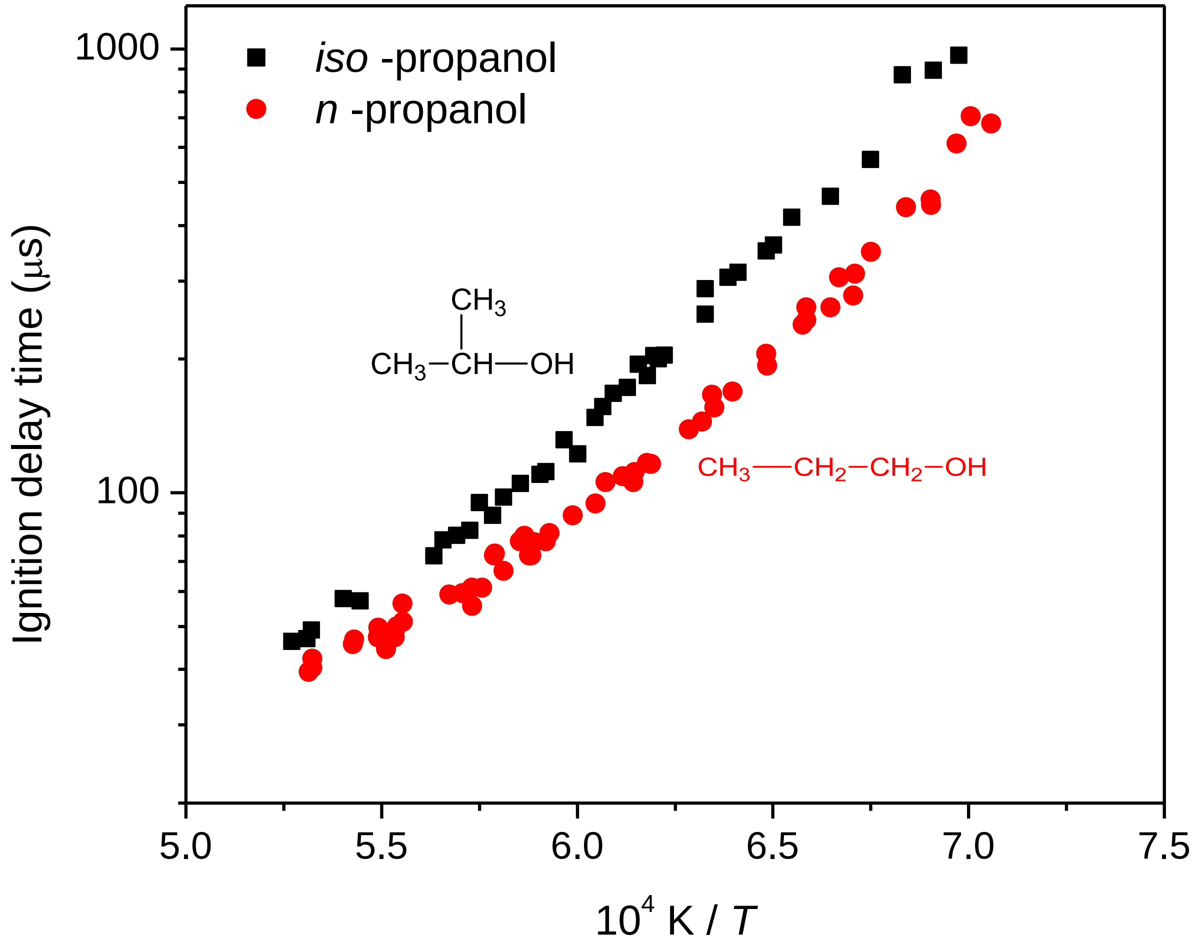
chain
branching

Intermediate temperature

Fuel decomposition reactions

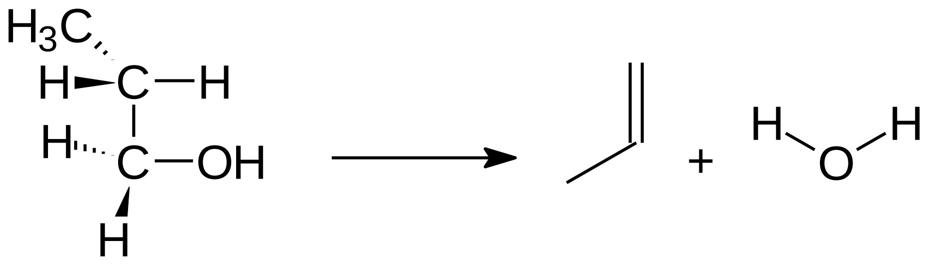
Propanol isomers: Comparison of reactivity

0.5% fuel, 2.25% O_2, $\phi = 1.0$, P = 1 atm



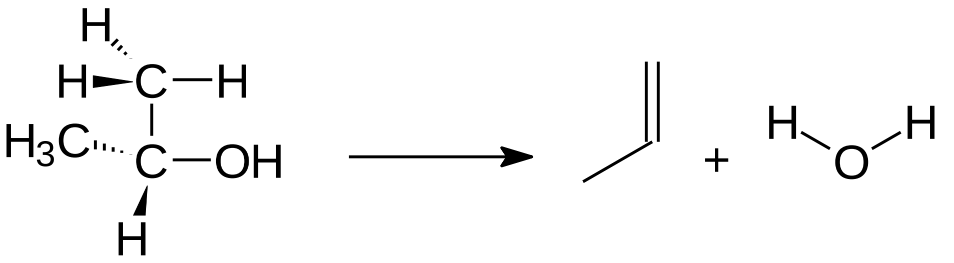
Johnson *et al.* Energy & Fuels (2009) *23* 5886–5898.

Alcohol molecular elimination



n-propanol propene + water

$k = 3.52 \times 10^{13}$ 0. 67300. s^{-1}

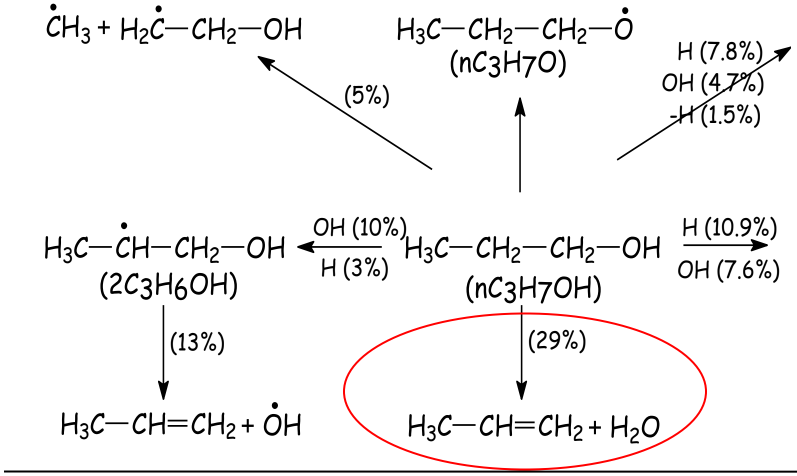


iso-propanol propene + water

$k = 2.11 \times 10^{14}$ 0. 67300. s^{-1}

Tsang, W. Int. J. Chem. Kinet. (1976) 8: 173–192.

Water elimination is much more important for iso-propanol



$\dot{C}H_3 + H_2\dot{C}-CH_2-OH$
$H_3C-CH_2-CH_2-\dot{O}$
(nC_3H_7O)
(5%)
H (7.8%)
OH (4.7%)
-H (1.5%)
$H_3C-\dot{C}H-CH_2-OH$
$(2C_3H_6OH)$
OH (10%)
H (3%)
$H_3C-CH_2-CH_2-OH$
(nC_3H_7OH)
H (10.9%)
OH (7.6%)
(13%)
(29%)
$H_3C-CH=CH_2 + \dot{O}H$
$H_3C-CH=CH_2 + H_2O$

0.5% *n*-propanol

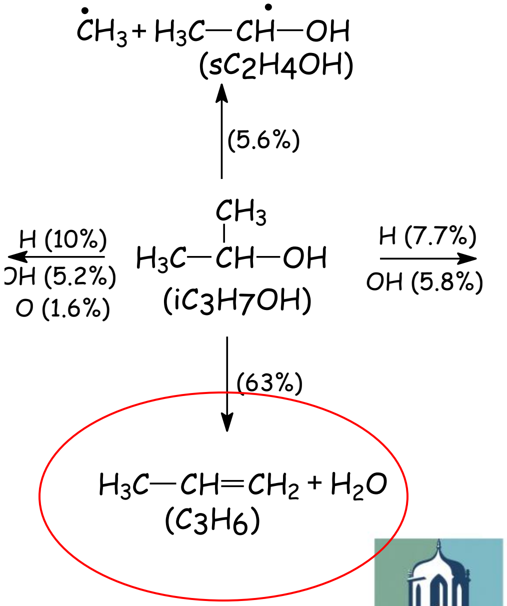
ϕ = 1.0, *T* = 1600 K

30% fuel consumed

0.5% *iso*-propanol

ϕ = 1.0, *T* = 1600 K

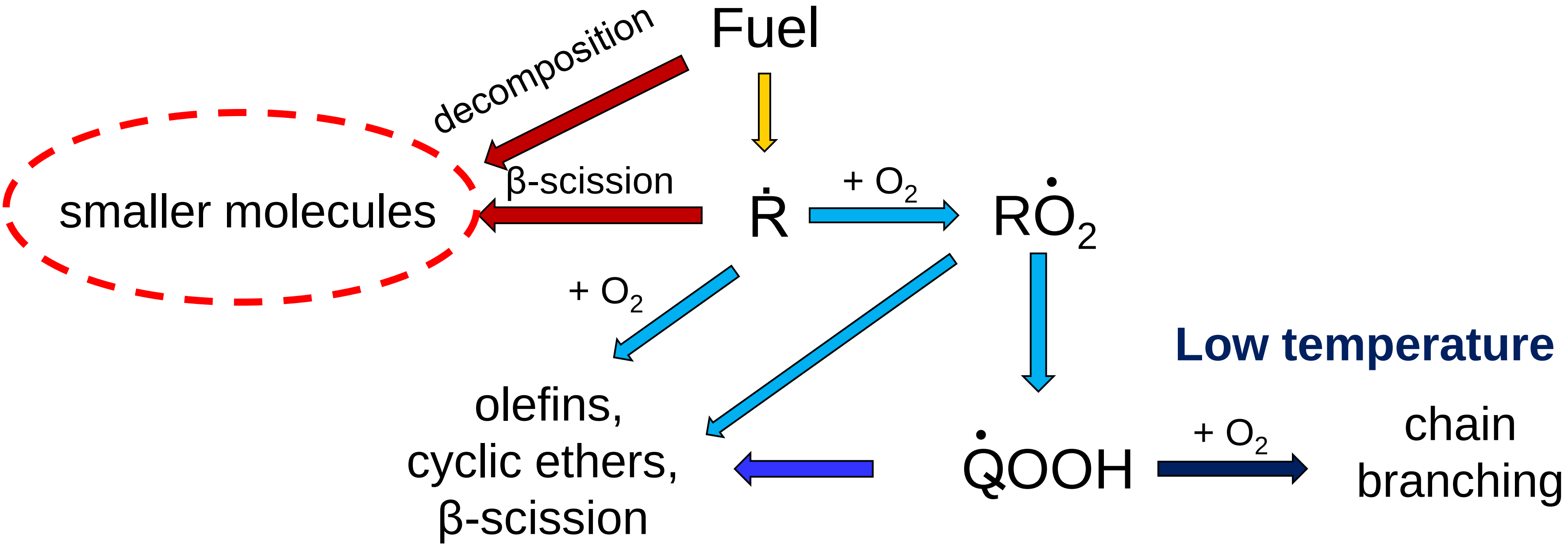
30% fuel consumed



$\dot{C}H_3 + H_3C-\dot{C}H-OH$
(sC_2H_4OH)
(5.6%)
CH_3
$H_3C-CH-OH$
(iC_3H_7OH)
H (10%)
OH (5.2%)
O (1.6%)
H (7.7%)
OH (5.8%)
(63%)
$H_3C-CH=CH_2 + H_2O$
(C_3H_6)

Johnson *et al.* Energy & Fuels (2009) *23:* 5886–5898.

General reaction scheme



High temperature

Fuel

decomposition

smaller molecules

β-scission

$\dot{R}$

+ O_2

$R\dot{O}_2$

+ O_2

olefins,
cyclic ethers,
β-scission

$\dot{Q}OOH$

+ O_2

chain
branching

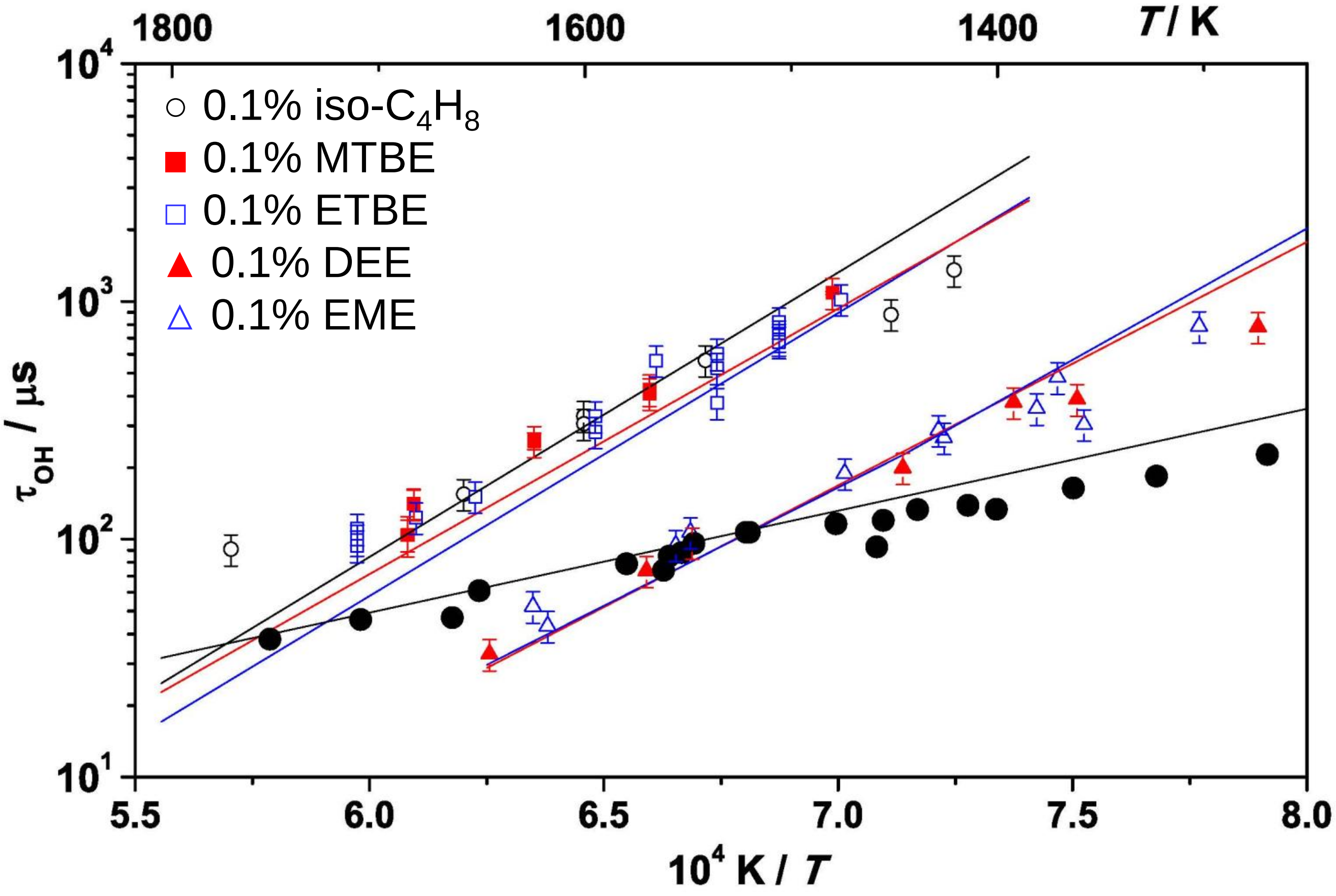
Low temperature

Intermediate temperature

Sub-mechanism

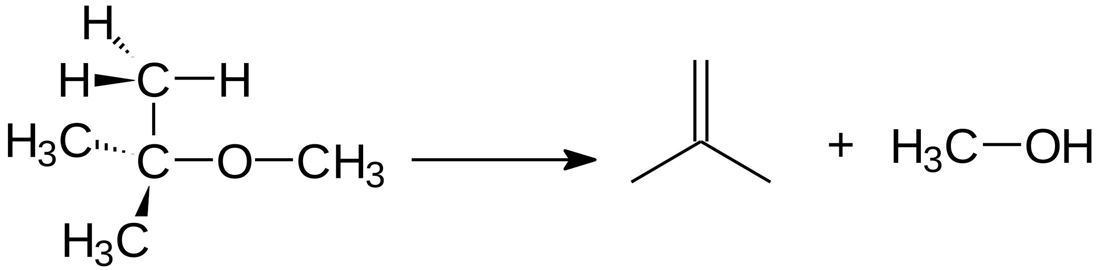
Reactivity of ethers

- **1% H_2, 1% O_2 in Ar, p_5 = 1.4–2.6 atm**



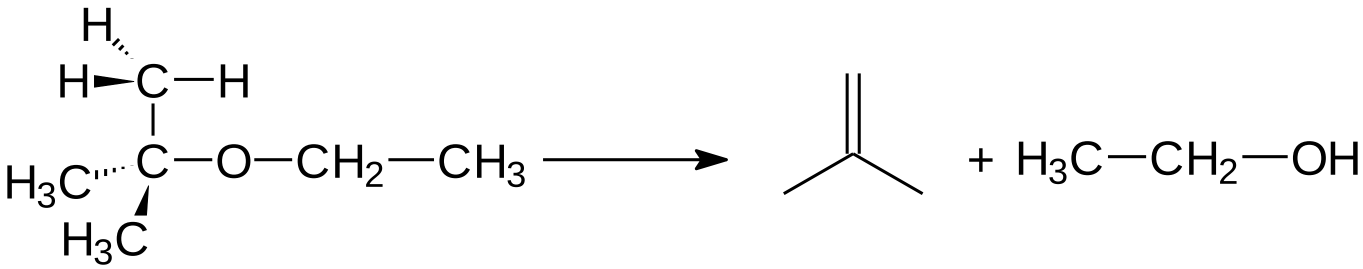
Yasunaga *et al.* Comb. Flame (2011) *158:* 1032–1036.

Ether molecular elimination



MTBE isobutene + methanol

$k = 1.70 \times 10^{14}$ 0. 60800. s^{-1}



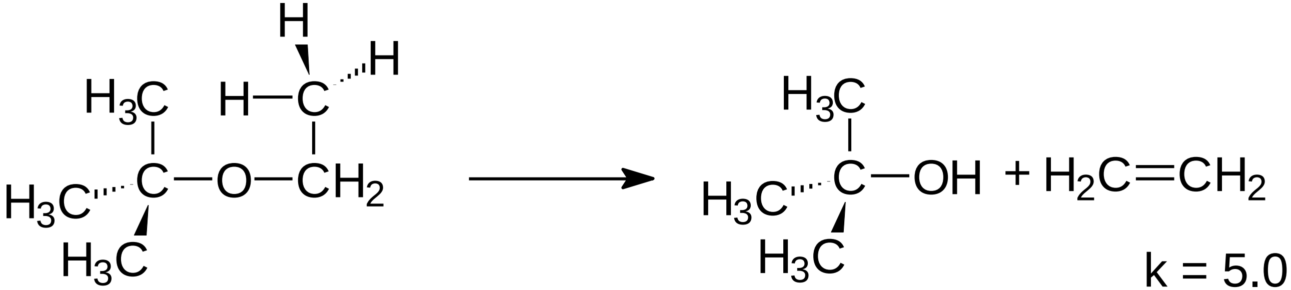
ETBE isobutene + ethanol

$k = 1.70 \times 10^{14}$ 0. 60600. s^{-1}

Yasunaga *et al.* Comb. Flame (2011) *158:* 1032–1036.

MP4/cc-pVTZ//MP2/cc-pVTZ level of theory with zero point corrections

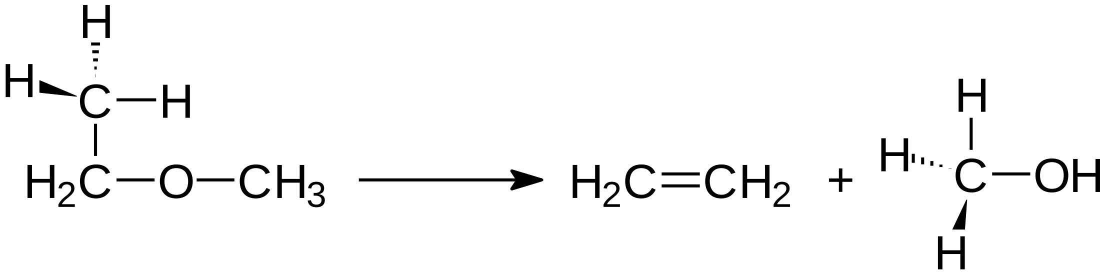
Ether molecular elimination



$k = 5.0 \times 10^{13}$ 0. 63400. s^{-1}

ETBE

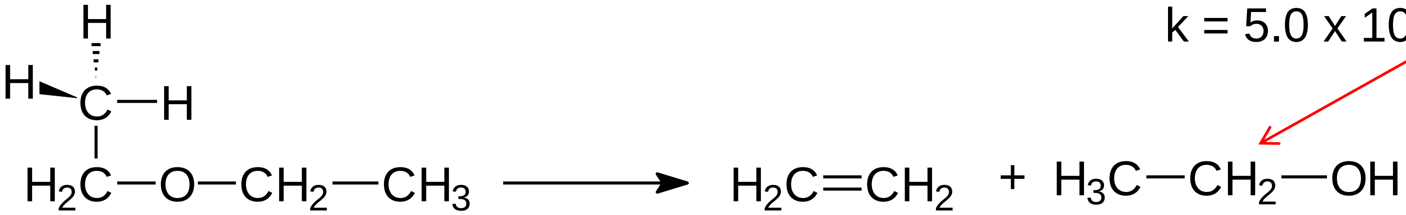
tert-butanol + ethylene



EME

ethylene + methanol

$k = 5.0 \times 10^{13}$ 0. 65200. s^{-1}



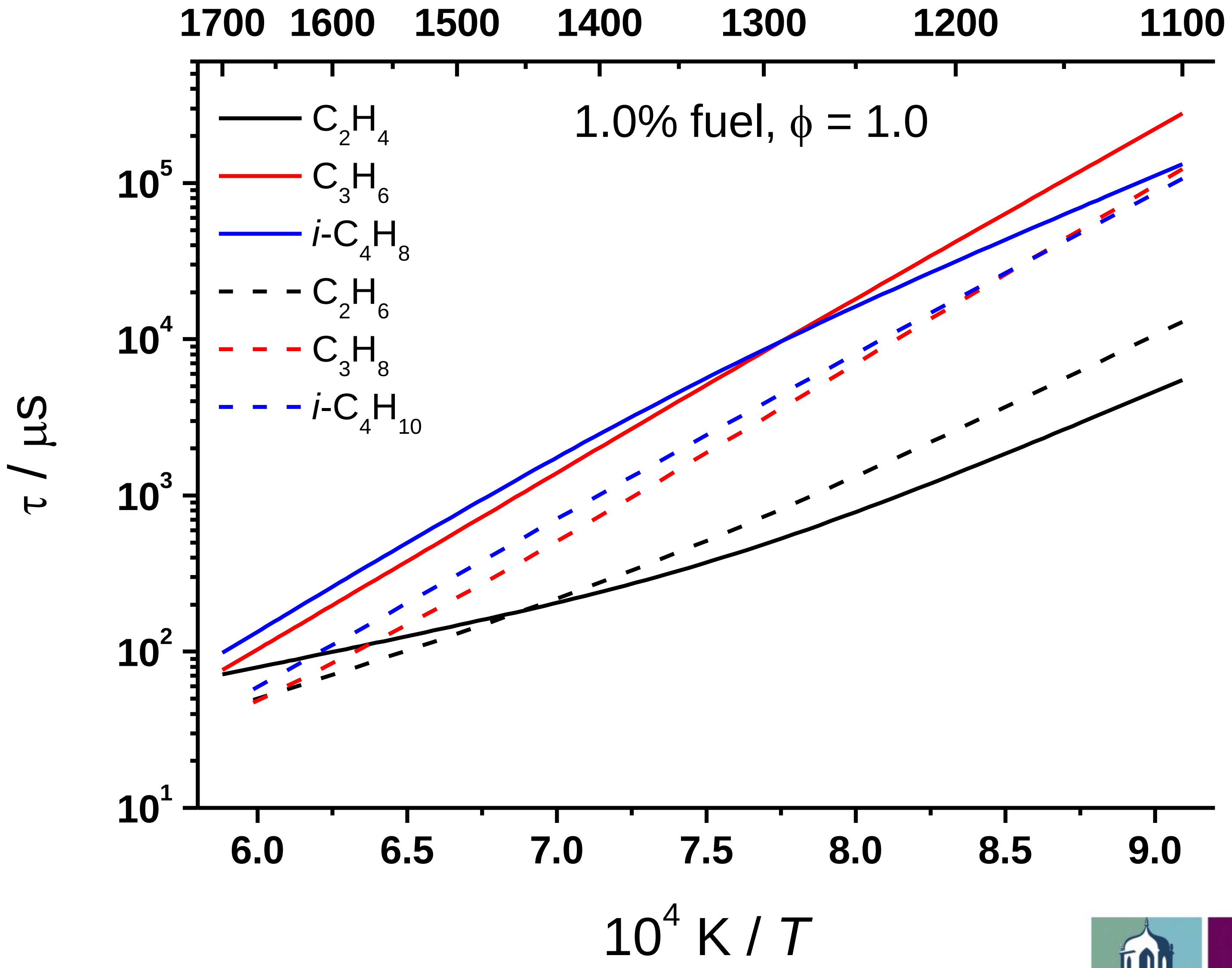
DEE

ethylene + ethanol

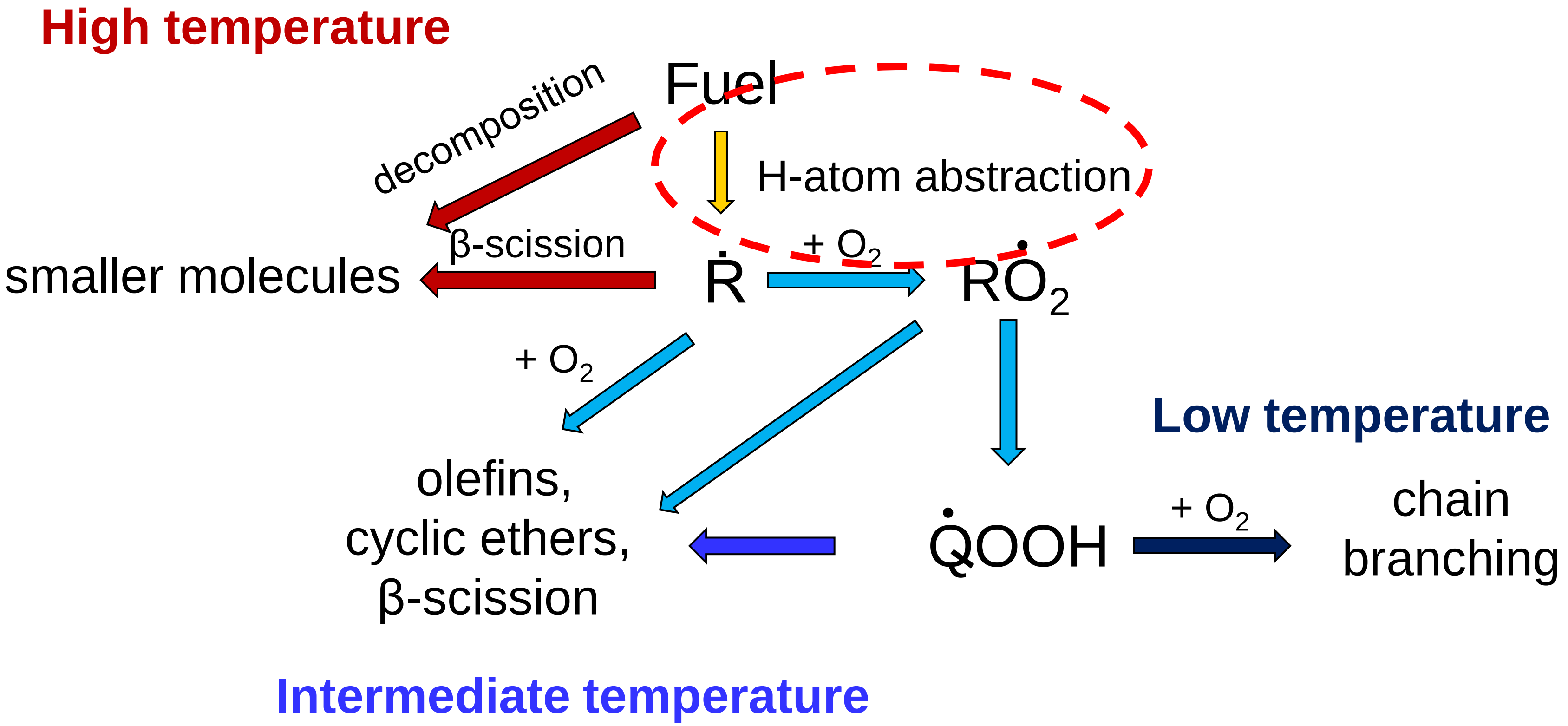
Yasunaga *et al.* Comb. Flame (2011) *158:* 1032–1036.

MP4/cc-pVTZ//MP2/cc-pVTZ level of theory with zero point corrections

Ethylene is very fast to ignite



General reaction scheme



High temperature

Fuel

decomposition

H-atom abstraction

β-scission

smaller molecules

$\dot{R}$

+ O_2

$R\dot{O}_2$

+ O_2

Low temperature

olefins,
cyclic ethers,
β-scission

$\dot{Q}OOH$

+ O_2

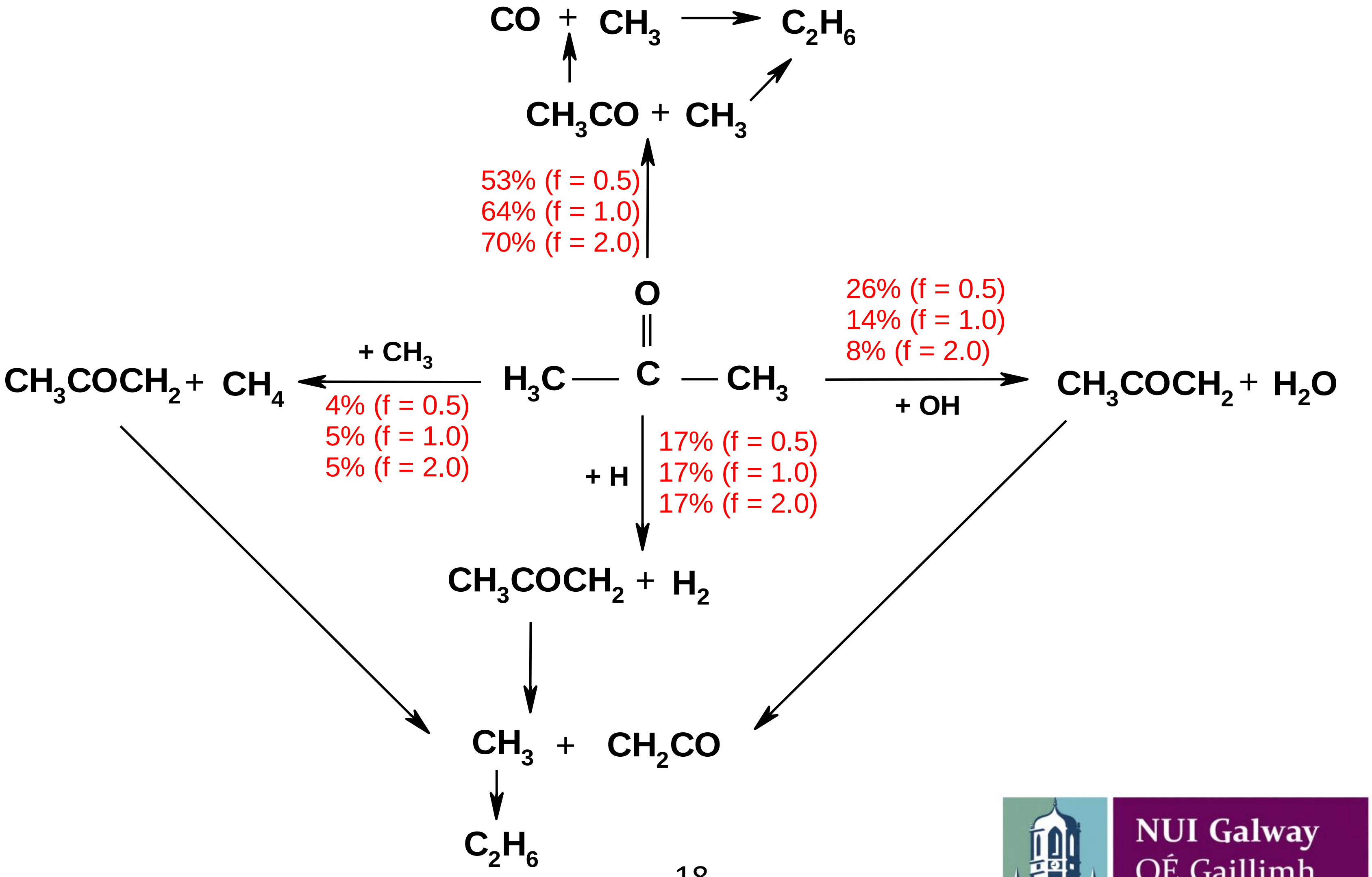
chain
branching

Intermediate temperature

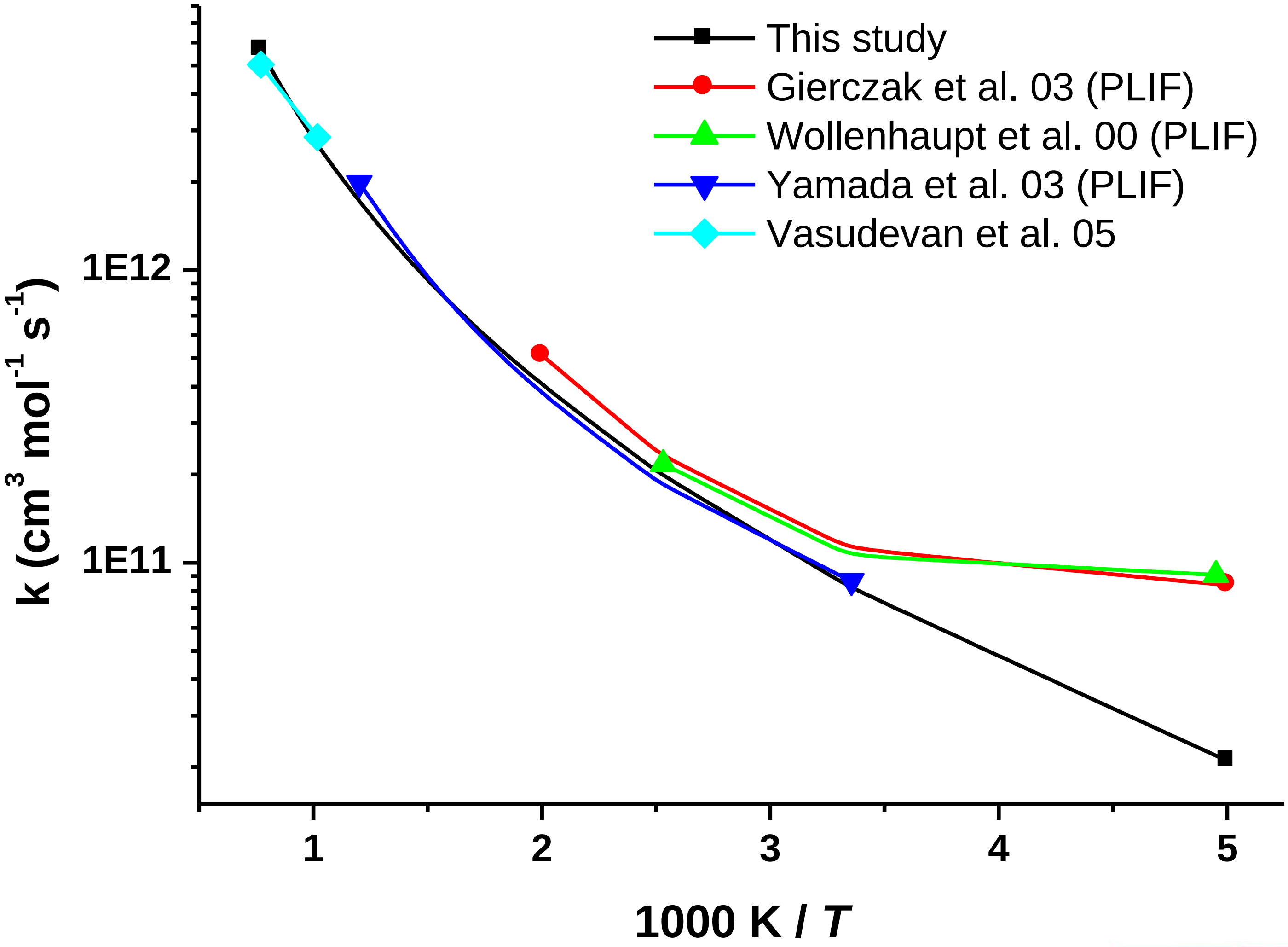
H-atom abstraction reactions

Acetone: Low *p*, High *T*

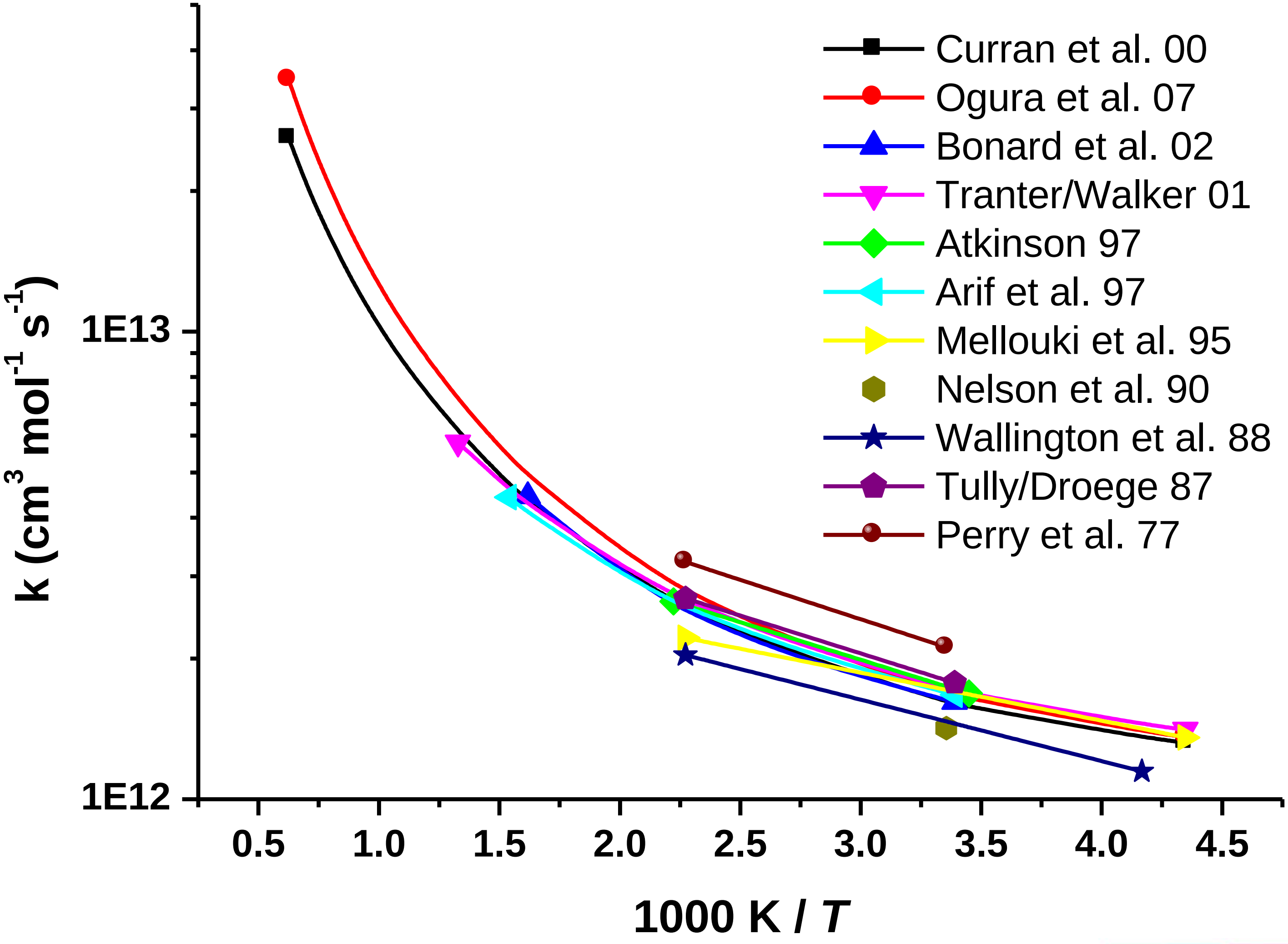
1.25% fuel, 22% fuel conversion, T = 1400 K, p = 1 atm


$CO + CH_3 \rightarrow C_2H_6$
$CH_3CO + CH_3$
53% (f = 0.5)
64% (f = 1.0)
70% (f = 2.0)
$H_3C-C(=O)-CH_3$
26% (f = 0.5)
14% (f = 1.0)
8% (f = 2.0)
+ OH
$CH_3COCH_2 + H_2O$
+ CH_3
$CH_3COCH_2 + CH_4$
4% (f = 0.5)
5% (f = 1.0)
5% (f = 2.0)
+ H
17% (f = 0.5)
17% (f = 1.0)
17% (f = 2.0)
$CH_3COCH_2 + H_2$
$CH_3 + CH_2CO$
C_2H_6

$CH_3COCH_3 + OH = CH_3COCH_2 + H_2O$

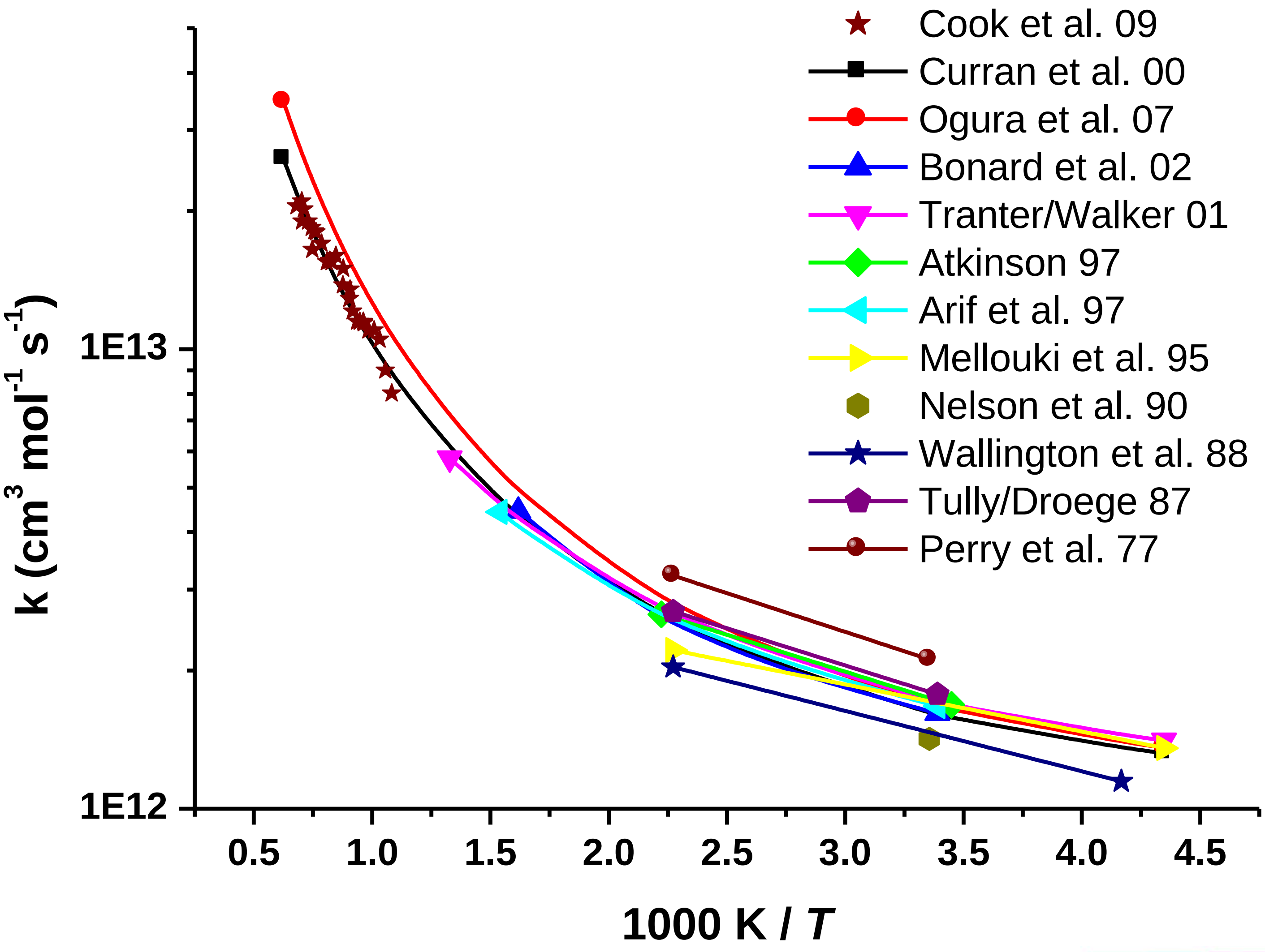


$CH_3OCH_3 + OH = CH_3OCH_2 + H_2O$



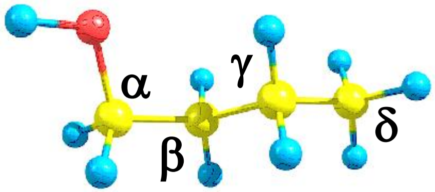
NUI Galway
OÉ Gaillimh

$CH_3OCH_3 + OH = CH_3OCH_2 + H_2O$



H-atom Abstraction

- *n*-Butanol + •OH/HO_2•

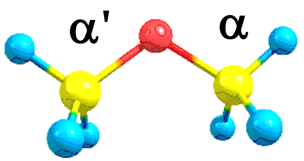


C-W. Zhou, J. M. Simmie, H. J. Curran. *Combust. & Flame*, **2011** *158* 726−731.
C-W. Zhou, J. M. Simmie, H. J. Curran. *Int. J. Chem. Kinet.*, **2012** *44* 155−164.

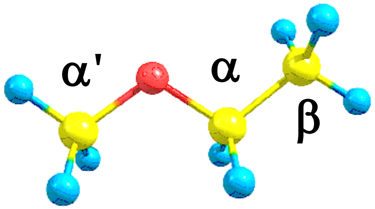
- *n*-Butanol + $\dot{C}H_3$ (Imperial College London: Prof. Alex Taylor)

D. Katsikadakos, C-W. Zhou, J. M. Simmie, H. J. Curran, P.A. Hunt,
Y. Hardalupas, A.M.K.P. Taylor. *Proc. Comb. Inst.,* 2012. Paper 4D03 Thursday 2nd August.

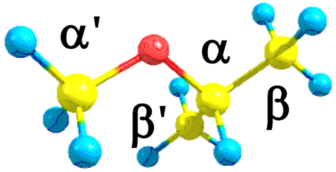
- Ethers + •OH



DME



EME

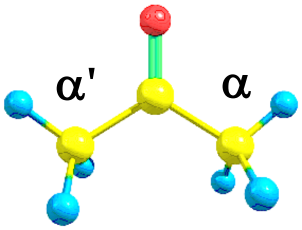


iPME

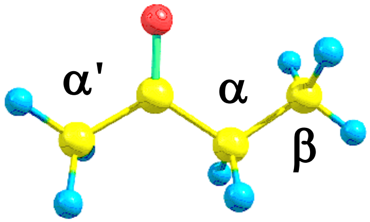
C-W. Zhou, J.M. Simmie, H.J. Curran
Phys. Chem. Chem. Phys. **2010** *12* 7221−7233.

H-atom Abstraction

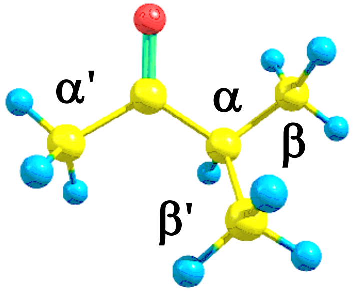
- Ketones + •OH



DMK



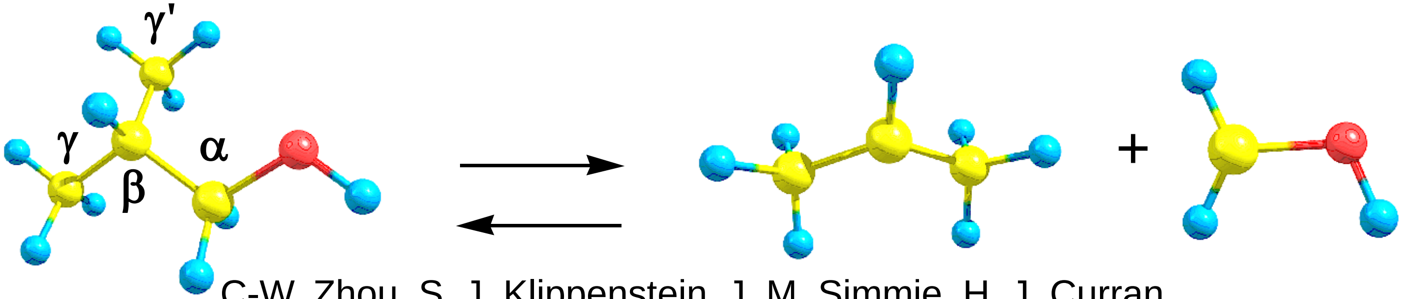
EMK



iPMK

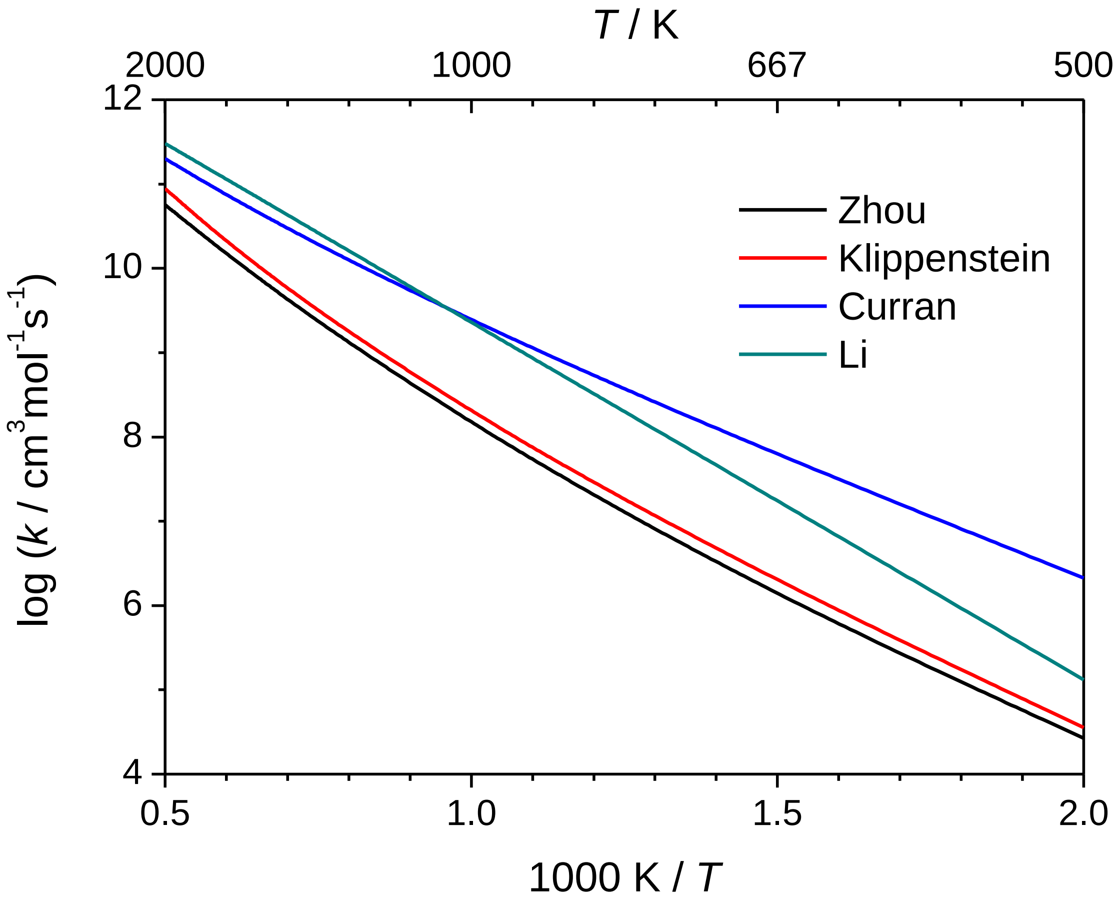
C-W. Zhou, J. M. Simmie, H. J. Curran. *Phys. Chem. Chem. Phys*. **2011** *13* 11175−11192.

- *iso*-Butanol decomposition and related $(CH_3)_2\dot{C}H + \dot{C}H_2OH$ reaction (Argonne National Laboratory: Dr. Stephen Klippenstein)



C-W. Zhou, S. J. Klippenstein, J. M. Simmie, H. J. Curran
Proc. Comb. Inst., **2012** *in press*
Paper : 4D05 Thursday 2nd August

$CH_3OH + H\dot{O}_2 \longrightarrow \dot{C}H_2OH + H_2O_2$



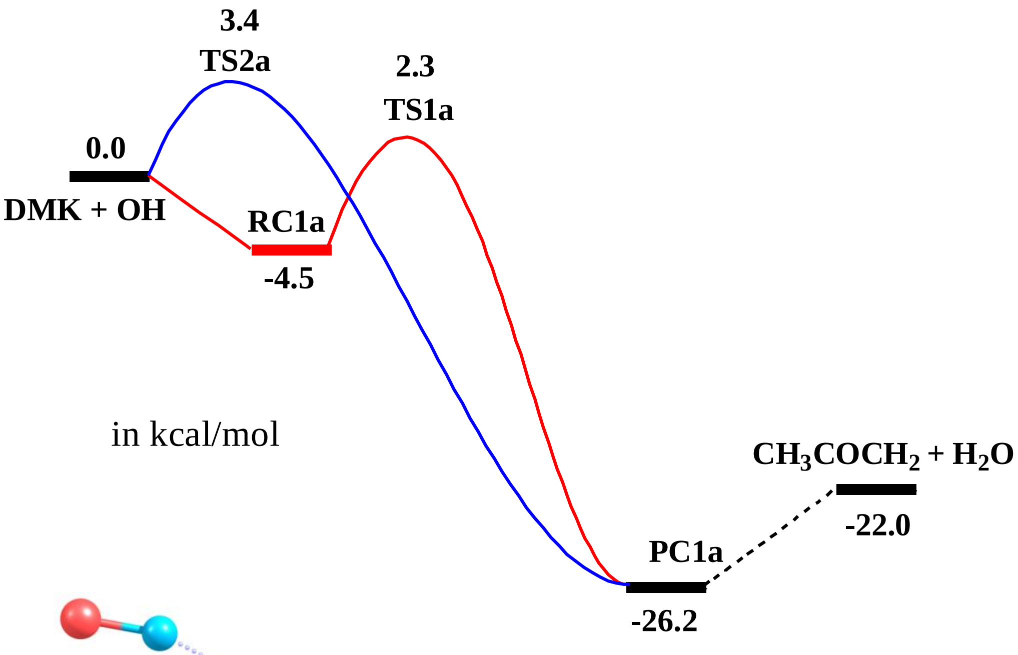
	A	*n*	*E*
Zhou	6.24E-05	4.89	1.05E+04
Klippenstein	2.28E-05	5.06	1.02E+04
Curran	1.08E+04	2.55	1.05E+04
Li	3.98E+13	0.00	1.94E+04

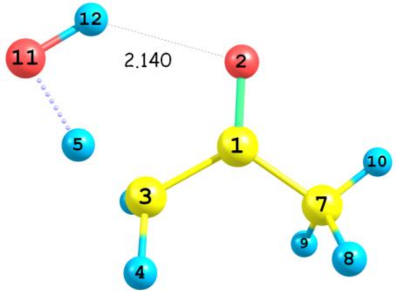
$$k = AT^{n}\exp(-E/\mathrm{R}T)$$

--- in cm^3, mol, s, cal units

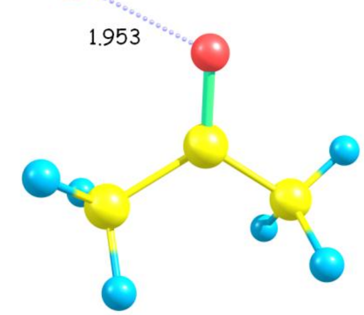
Klippenstein, S J.; Harding, L B.; Davis, M J. *et al.* Proc. Comb. Inst. **2011** *33* 351−358.
Li, J.; Zhao, Z.; Kazakov, A.; Chaos, M.; Dryer, F L. et al. Int. J. Chem. Kinet. **2007** *39* 109−136.

Acetone: α' hydrogen reactivity

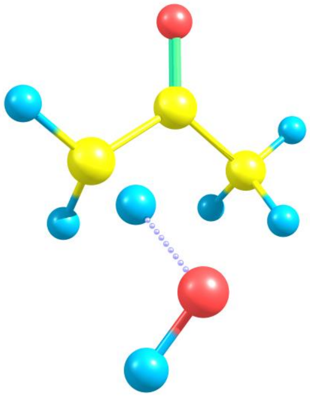



12
11
2.140
2
5
1
10
3
7
9
8
4

TS1a

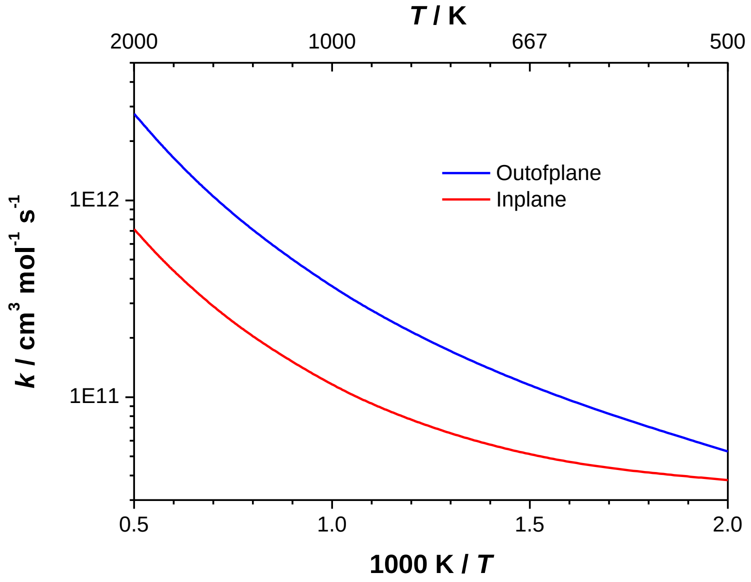


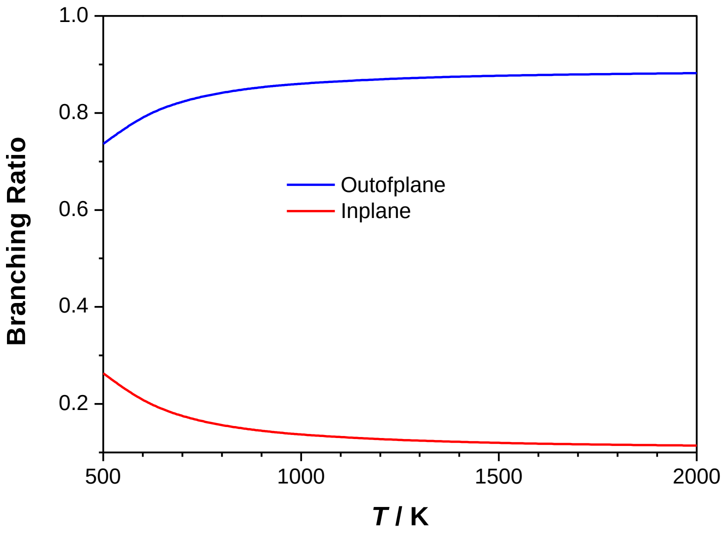
RC1a

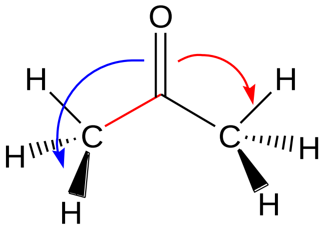


TS2a

Acetone: α' hydrogen reactivity





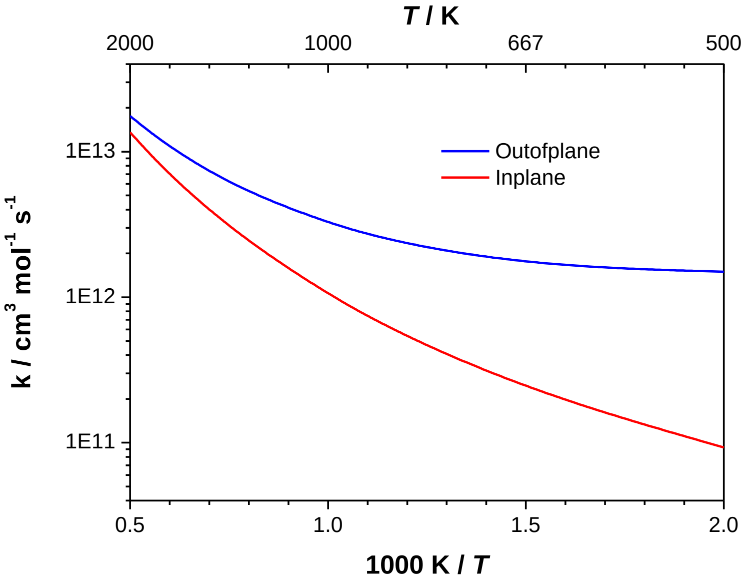


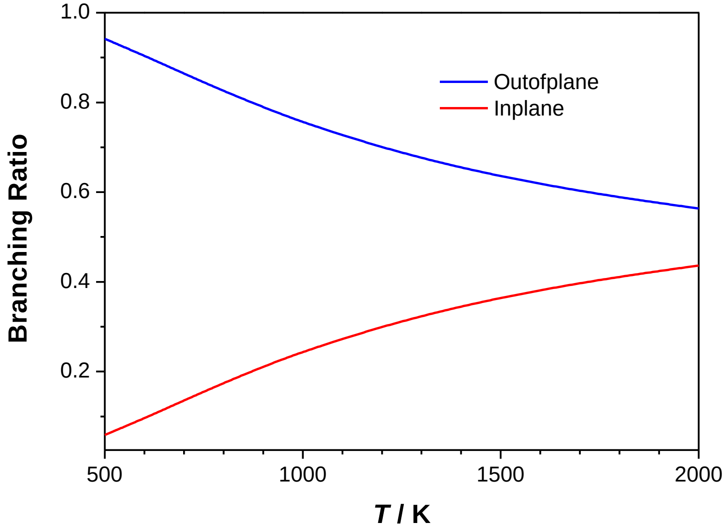
- Electron delocalization from π(CO) to σ*(CH_{in}) and σ*(CH_{out}) is different

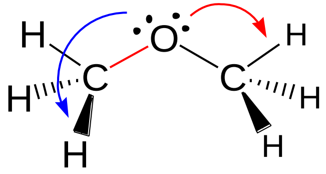
ΔE_{CT} = 2.0 kcal/mol

ΔE_{CT} = 0.0 kcal/mol

α' hydrogen reactivity in DME





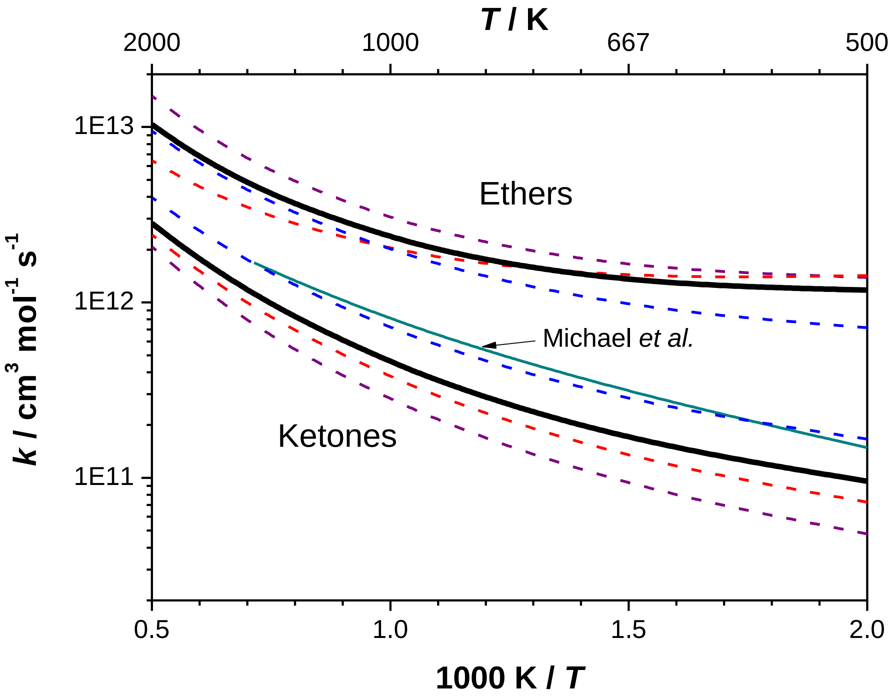


ΔE_{CT} = 4.9 kcal/mol

ΔE_{CT} = 1.7 kcal/mol

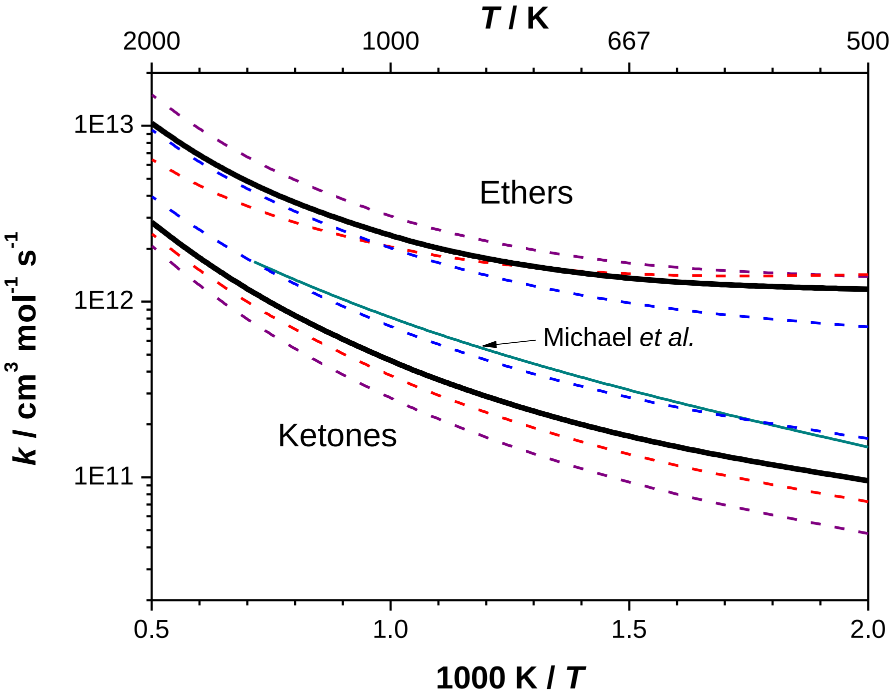
- Electron delocalization from oxygen lone pairs to σ*(CH_{out}) weaken the BDE of out-of-plane CH bond by 5.0 kcal/mol.

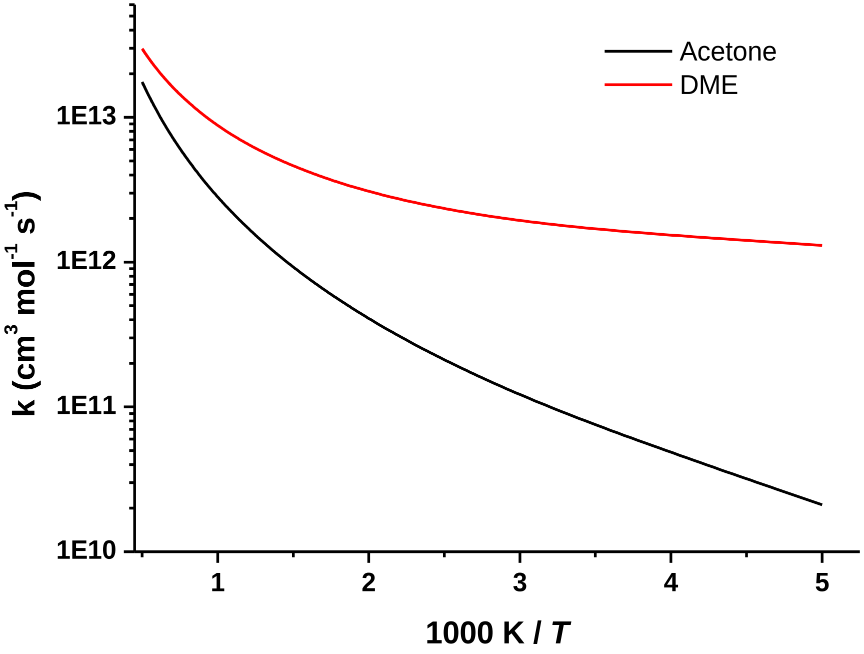
α' Reactivity Compared to Alkanes



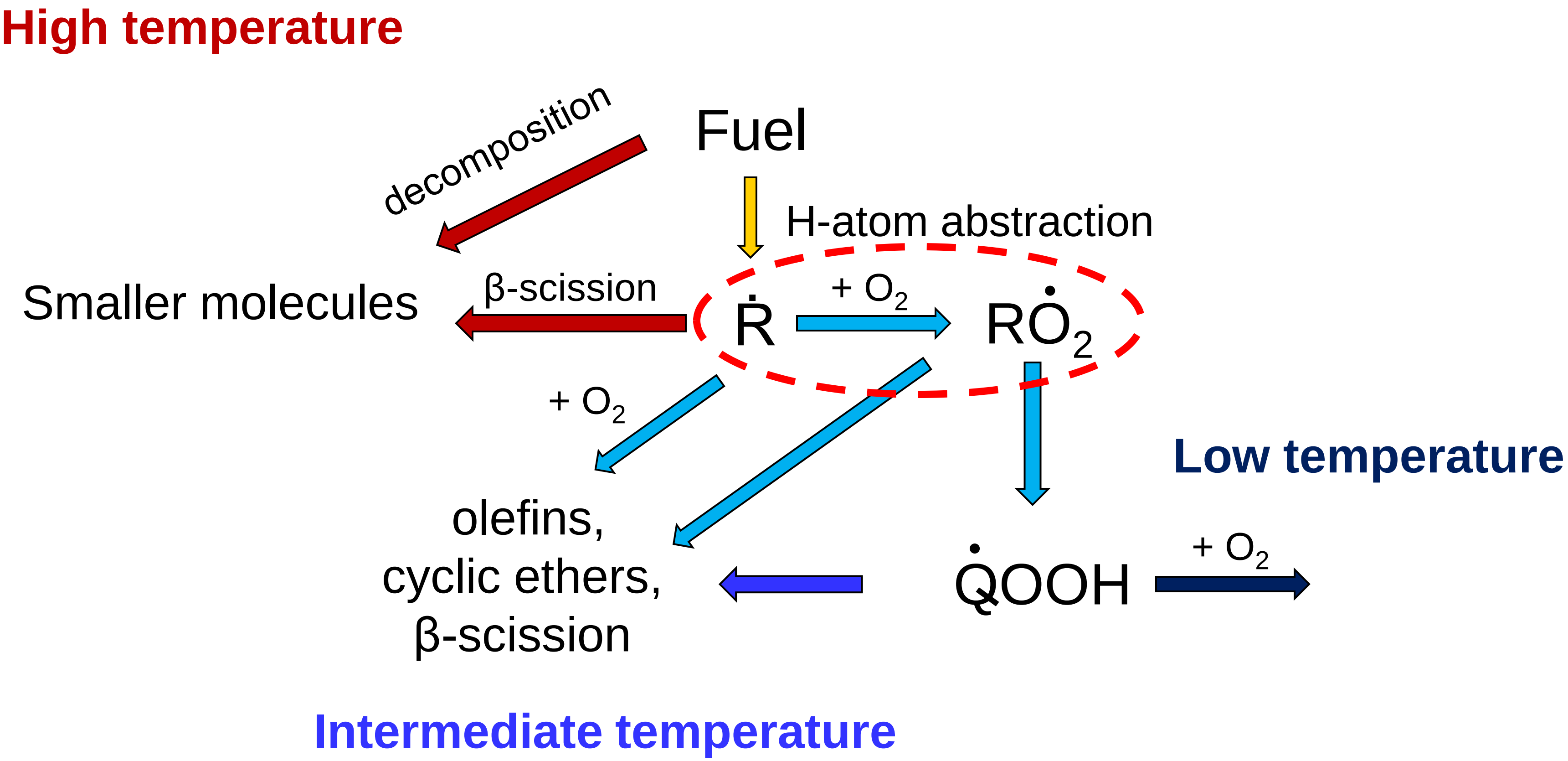
- Ethers
  - Oxygen lone pairs accelerate reactivity of α’ hydrogen compared to alkane
  - Growing size of the α-side has no influence on reactivity of α’ hydrogen atoms
- Ketones
  - α’ H-atom is less reactive than primary H-atom in alkanes
  - Growing size of the α-side will accelerate reactivity of α’ H-atoms

Comparative Reactivity





General reaction scheme

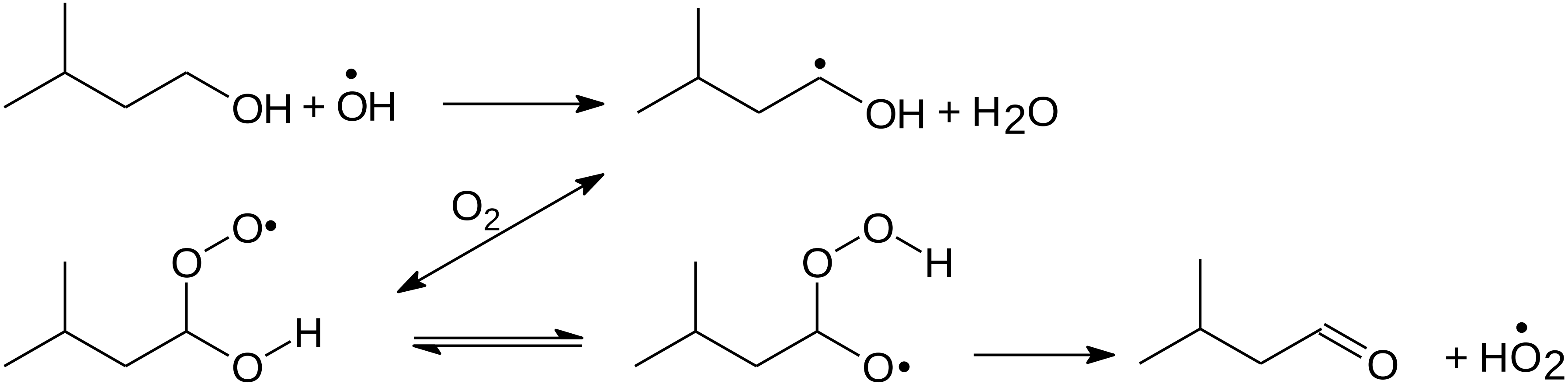

High temperature
decomposition
Fuel
H-atom abstraction
Smaller molecules
β-scission
Ṙ
+ O_2
R$\dot{O}_2$
+ O_2
Low temperature
olefins,
cyclic ethers,
β-scission
$\dot{Q}$OOH
+ O_2
Intermediate temperature

Low-temperature chemistry

NUI Galway
OÉ Gaillimh

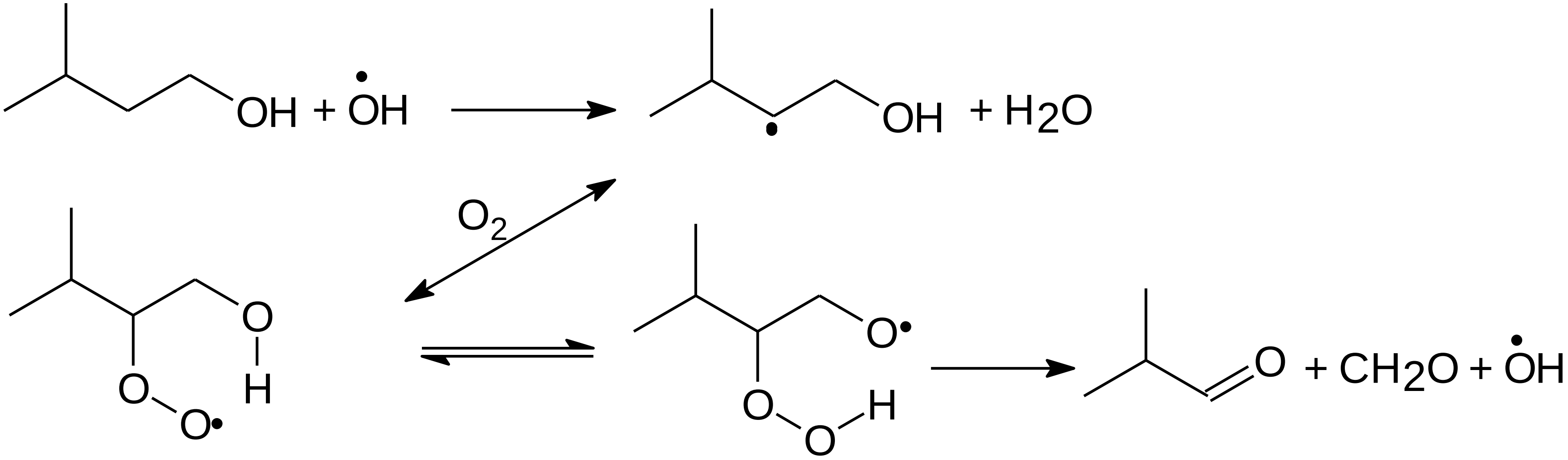
Alcohol Oxidation

Aldehyde formation from α-radical + O_2

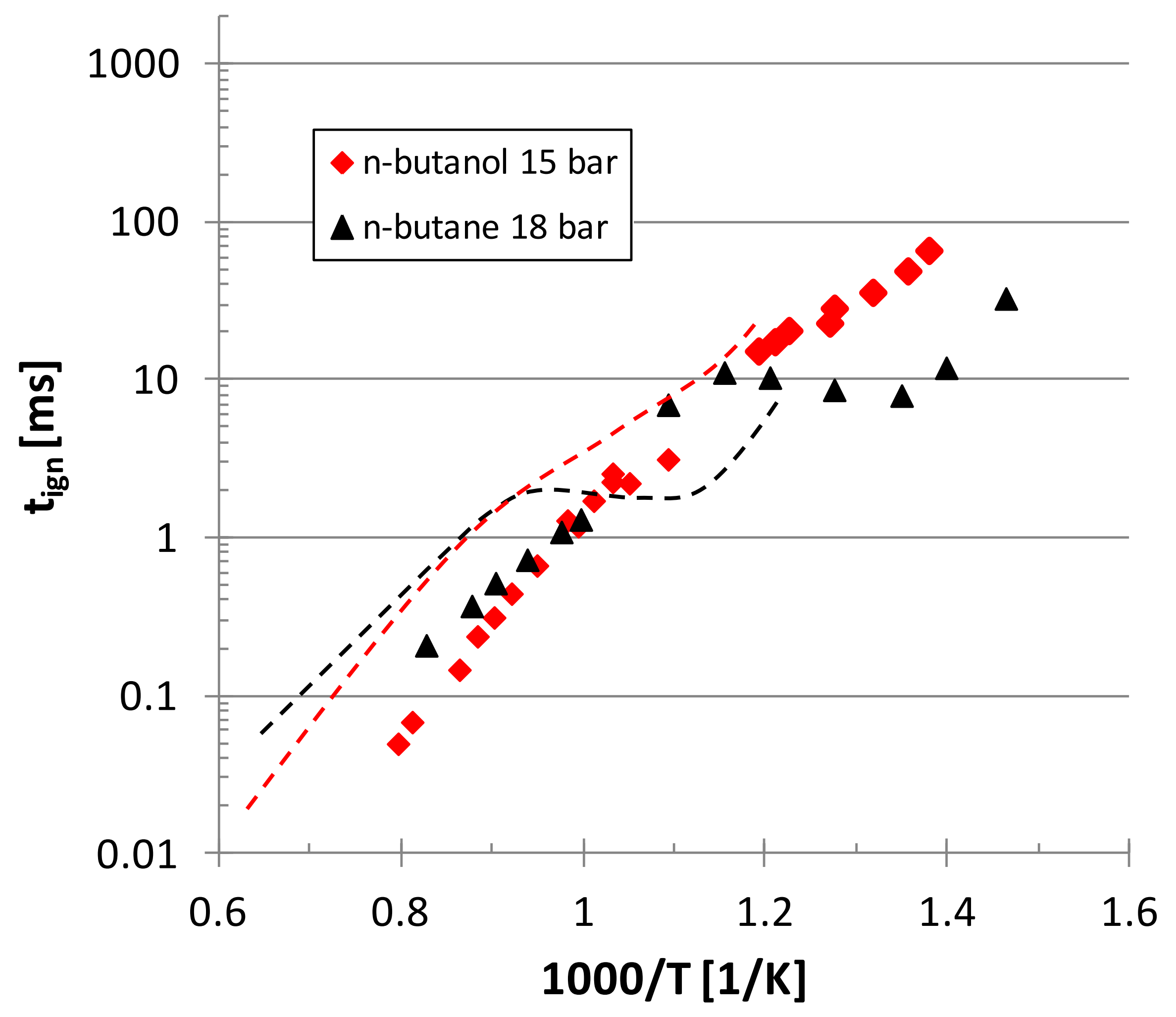

OH + ȮH
OH + H2O
O2
O•
O
H
O
O
H
O
O•
O
+ HȮ2

Alcohol Oxidation

Waddington mechanism (β-radical + O_2)


OH + •OH
OH + H_2O
O_2
O
H
O
O•
O•
O
O
H
O + CH_2O + •OH

Comparison: Alcohol/Alkane Oxidation

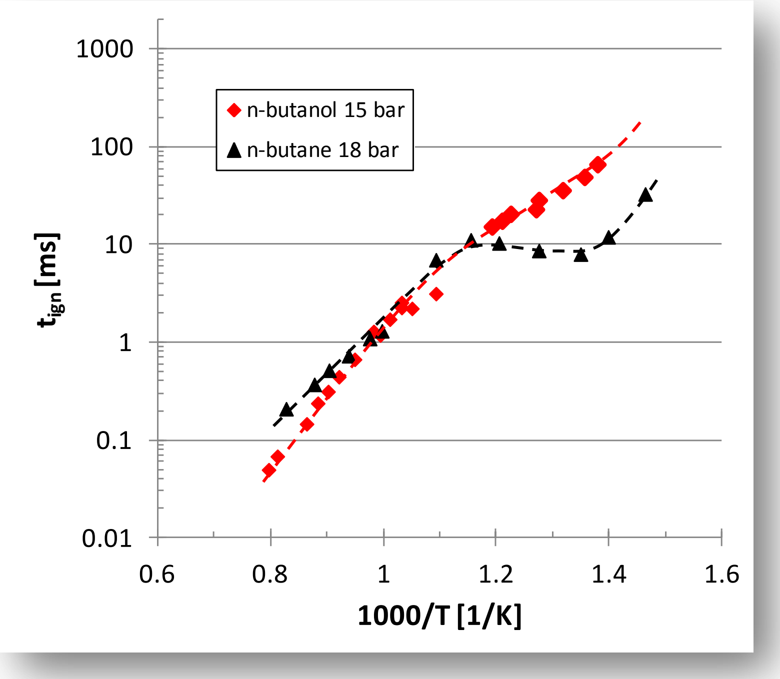


Effect of chain length

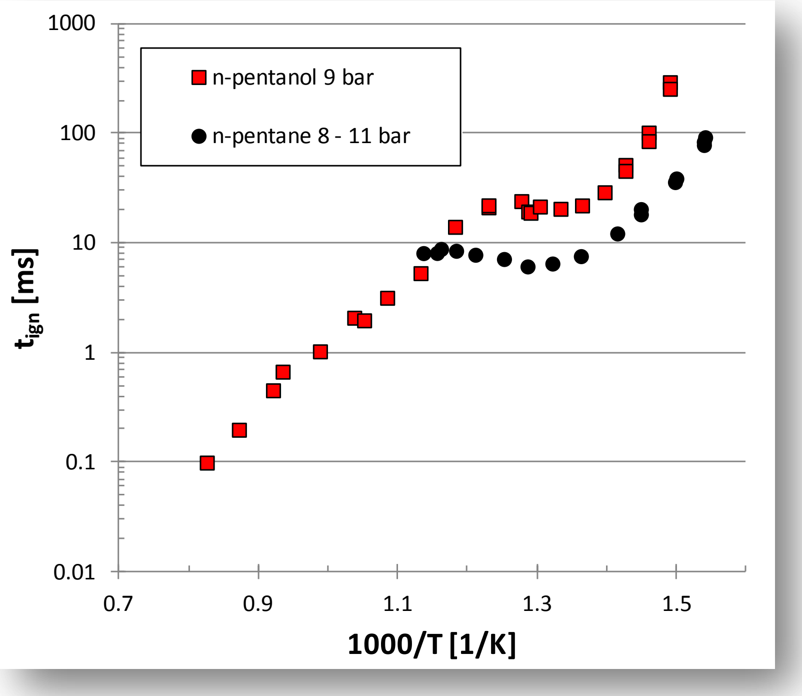
Alcohol Oxidation

Effect of chain length on influence of functional group

n-Butanol vs *n*-Butane

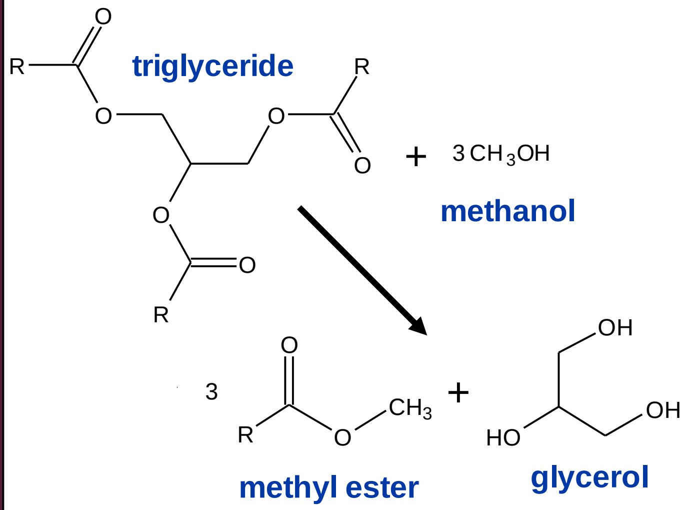


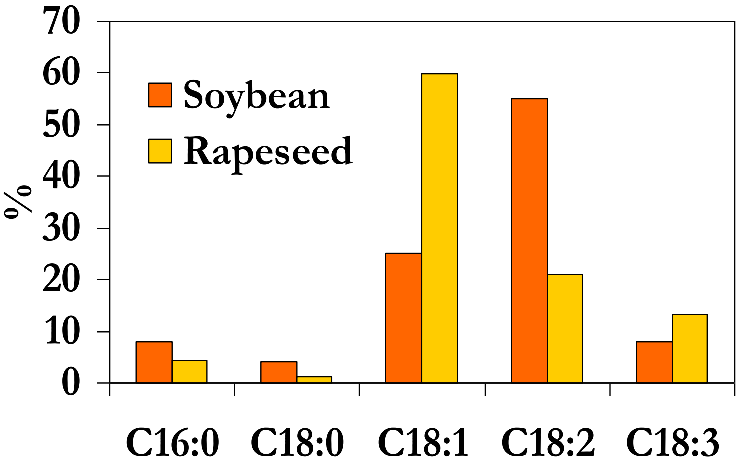
n-Pentanol vs *n*-Pentane



Heufer *et al.* Proc. Comb. Inst. (2012) in press.
Paper 4D06, Thursday 2nd August

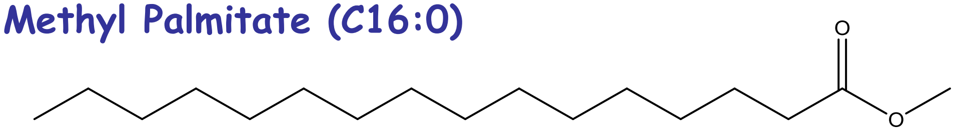
Soybean and rapeseed derived biodiesels have only 5 principal components


O
R
triglyceride
R
O
O
O
+
3 CH$_3$OH
methanol
O
O
R
3
O
R
O
CH$_3$
+
OH
HO
OH
methyl ester
glycerol

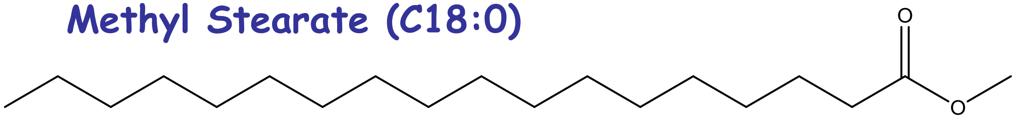


Fatty acid methyl esters (FAMEs):

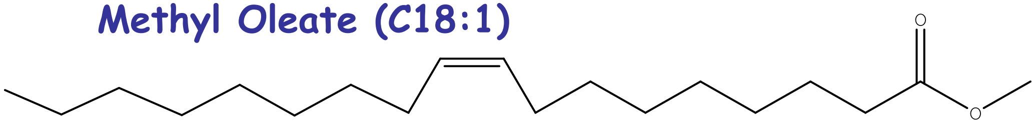
Methyl Palmitate (C16:0)



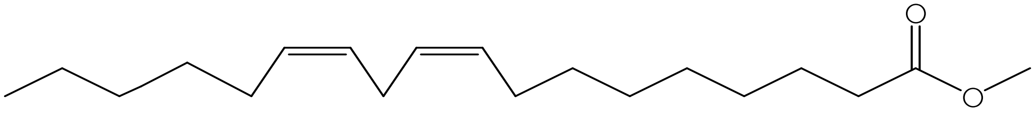
Methyl Stearate (C18:0)



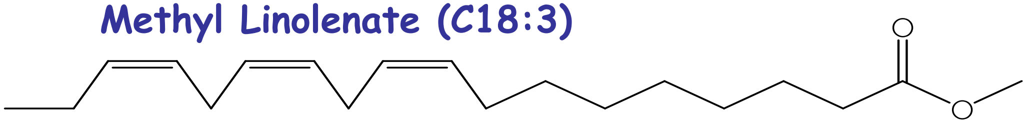
Methyl Oleate (C18:1)



Methyl Linoleate (C18:2)



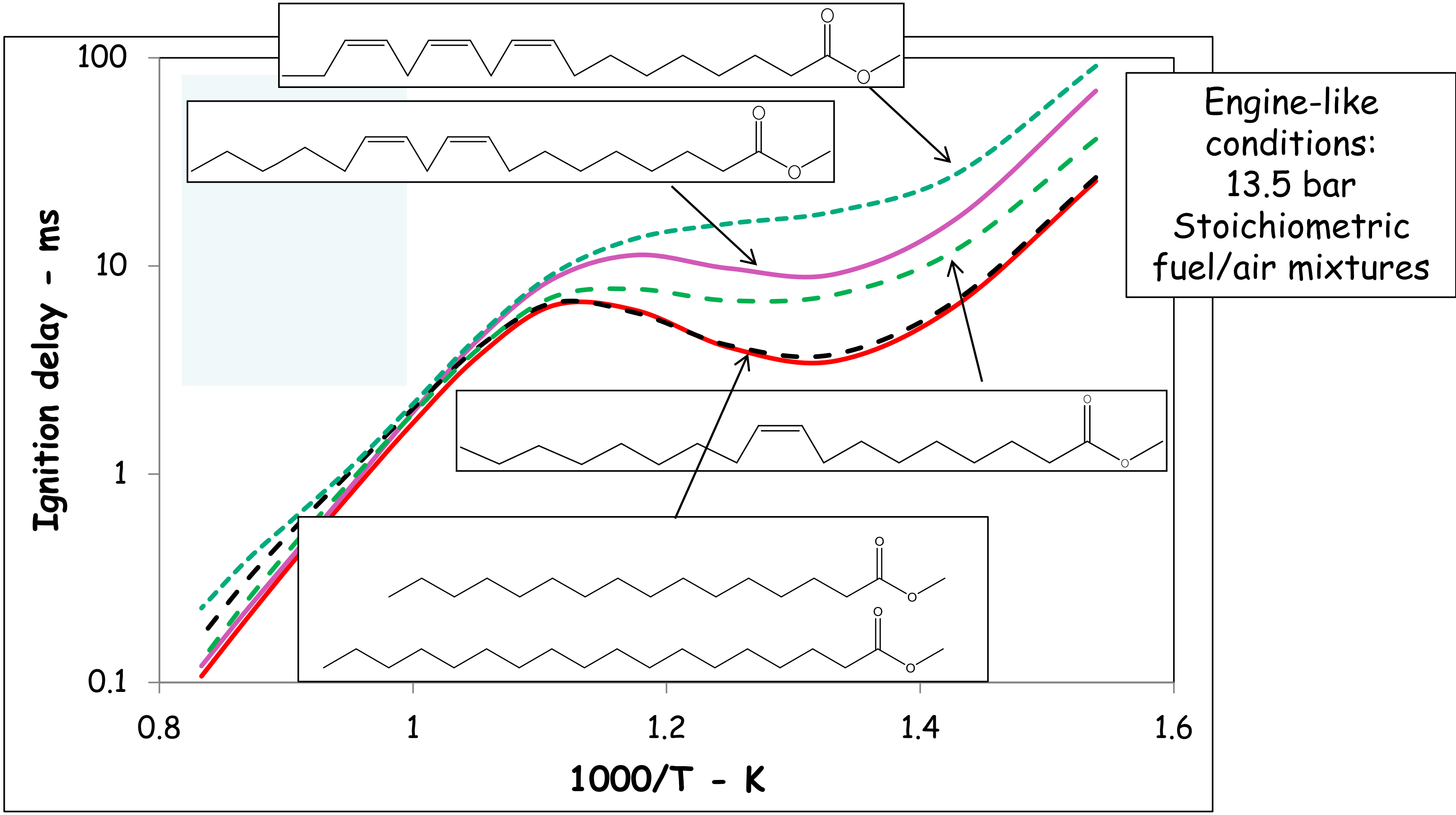
Methyl Linolenate (C18:3)



Westbrook *et al.* Proc. Comb. Inst. (2012) in press.

Paper 3D03 Wednesday 1st August

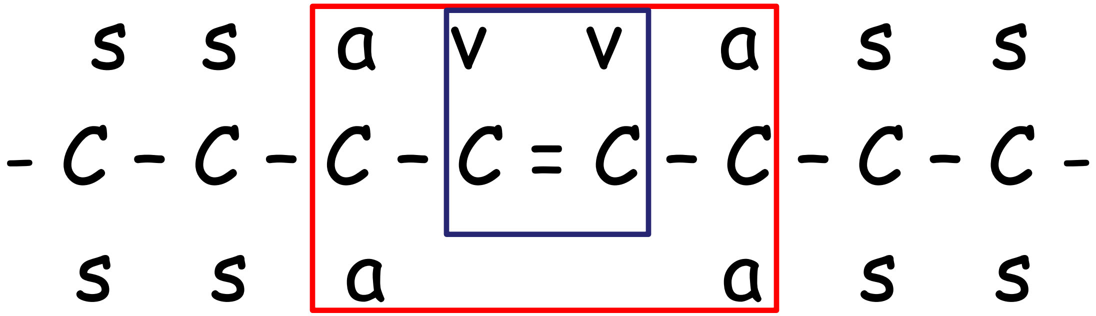
Biodiesel components ignite in order of number of double bonds



Westbrook *et al.* *Proc.* Comb. Inst. (2012) in press.

Paper 3D03 Wednesday 1st August

C = C double bonds reduce low T reactivity



s s a v v a s s

- C - C - C - C = C - C - C - C -

s s a a s s

- Inserting one C=C double bonds changes the reactivity of 4 carbons atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O$_2$ is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity

Westbrook *et al. Proc.* Comb. Inst. (2012) in press.
Paper 3D03 Wednesday 1st August

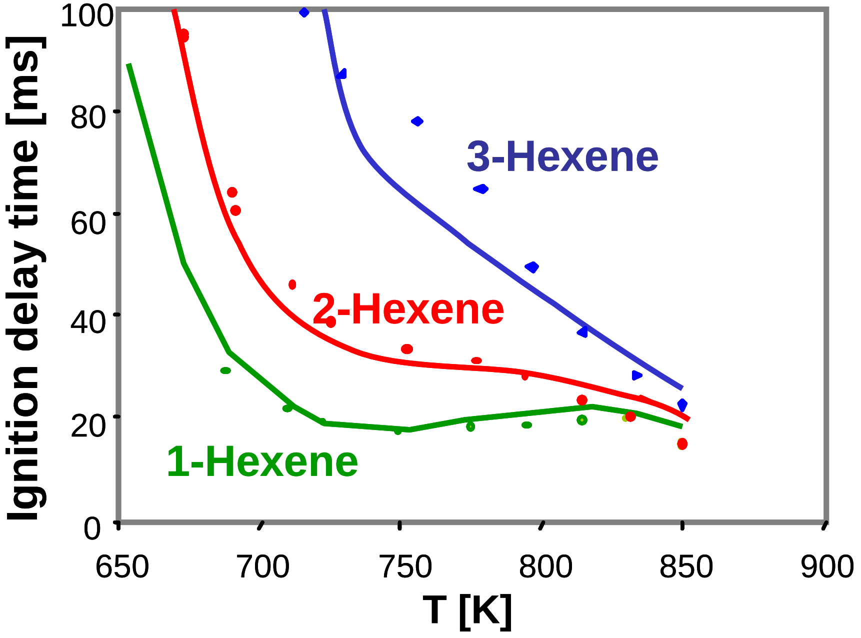
Observed same effect in hydrocarbon fuels: hexenes

C = C - C - C - C - C	1-hexene
C - C = C - C - C - C	2-hexene
C - C - C = C - C - C	3-hexene

RO_2 isomerization initiates low temperature reactivity

Moving the double bond towards the center of the molecule “inhibits” RO_2 kinetics

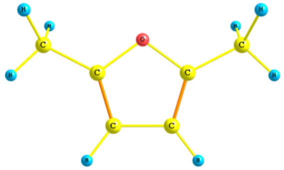
Ignition delay times in a rapid compression machine of hexene isomers (0.86-1.09 MPa, Φ=1):



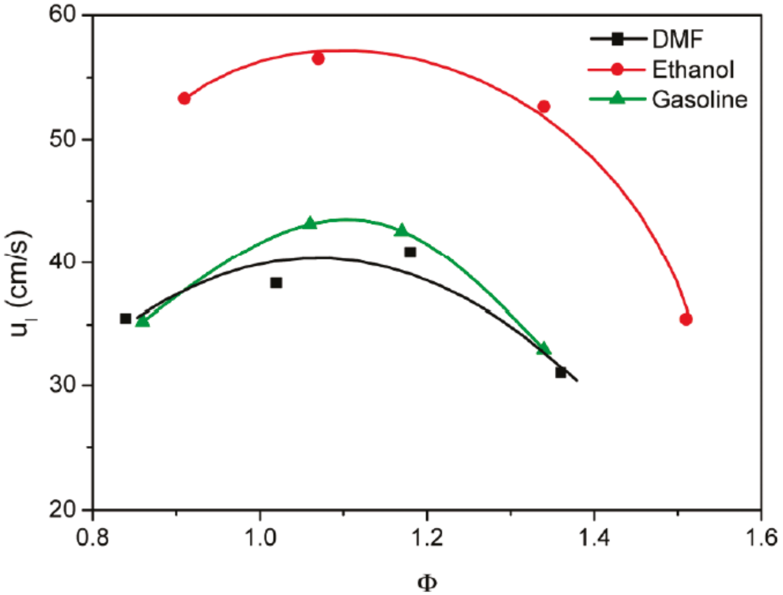
Experimental data: Vanhove et al. PCI 2005
Simulations: Mehl, Vanhove, Pitz, Ranzi Combustion and Flame 155 (2008) 756—772.

Novel fuels

Furans vs bio-ethanol



- Promising Next Generation Biofuels
  - Roman-Leshkov et al., Nature (2007) *447:* 982-985. (2nd generation)
- Novel renewable production process
  - Biomass (lignocellulosic) feedstock not destined for human/animal consumption
  - Highly efficient
  - Large scale and low cost
- Desirable physicochemical properties
  - Higher energy density (40%)
  - Direct combustion in unmodified engine
  - RON = 119
  - Lower aqueous solubility and less volatile



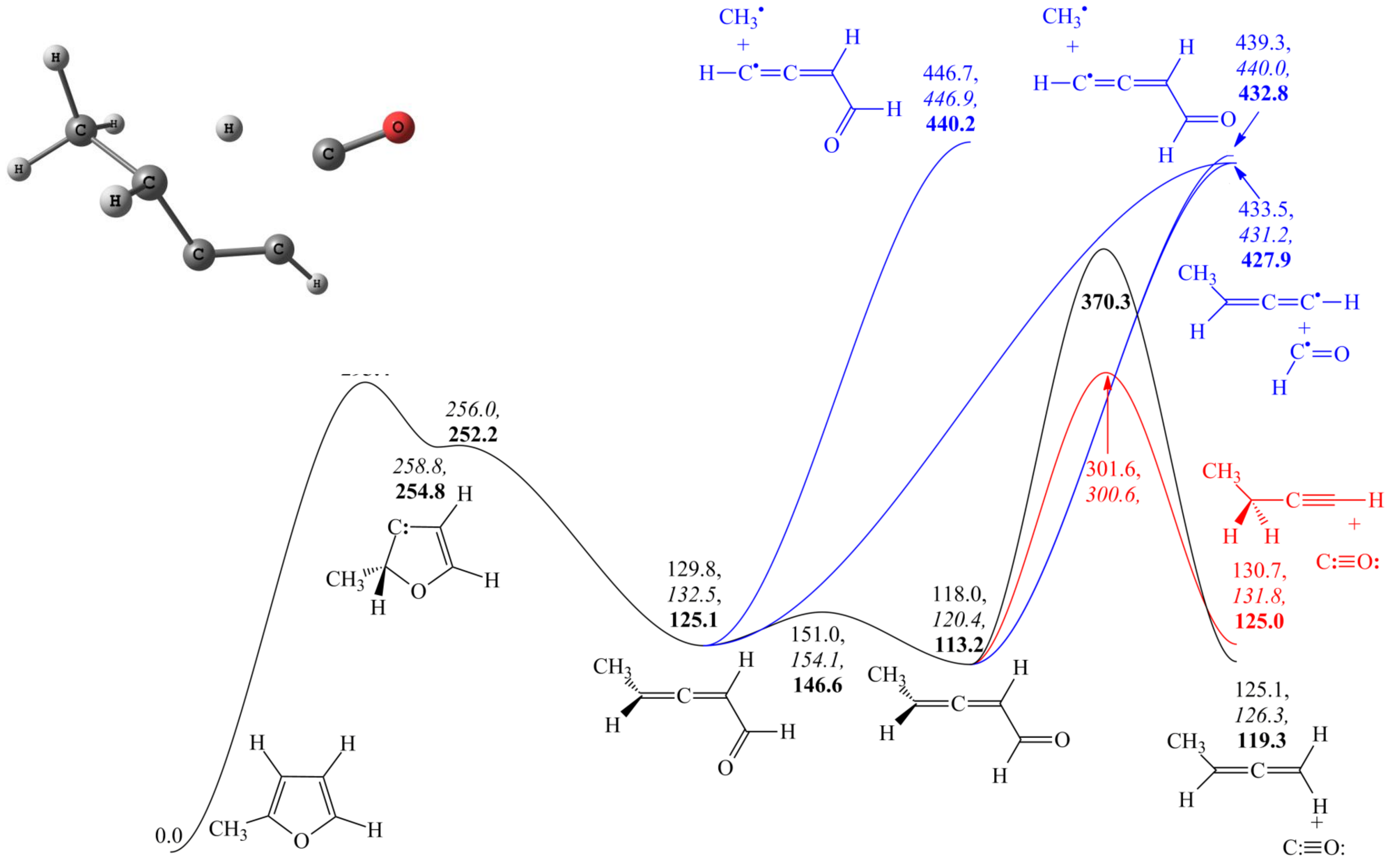
Laminar Flame Speed Measurements of DMF, Ethanol and Gasoline, Tian et al., Energy Fuels, **2010**

Energy Densities:

- Gasoline: 35 MJ/L
- 2,5-DMF: 31 MJ/L
- Bio-Ethanol: 23 MJ/L

Session 1: Monday morning: “Kinetics of Cyclic Ethers”

2MF: Unimolecular Decomposition



H
C
H
H
H
H
C
O
C
C
H
0.0
CH3
H
H
O
H
256.0,
252.2
258.8,
254.8
C:
H
CH3
O
H
H
129.8,
132.5,
125.1
CH3
C
H
H
O
H
151.0,
154.1,
146.6
118.0,
120.4,
113.2
CH3
C
H
H
O
H
CH3•
+
H—C•=C=
H
O
H
446.7,
446.9,
440.2
CH3•
+
H—C•=C=
H
O
H
439.3,
440.0,
432.8
433.5,
431.2,
427.9
CH3
=C=C•—H
H
+
C•=O
H
370.3
301.6,
300.6,
CH3
C≡—H
H H
+
C:≡O:
130.7,
131.8,
125.0
125.1,
126.3,
119.3
CH3
H
C
H
H
+
C:≡O:

Energies (0 K, kJ / mol) CBS-QB3, *CBS-APNO*, **G3**

Somers et al. Comb. Inst. (2012) in press. Paper1D01 Monday 30th July

Conclusions

- General chemical reaction schemes of HCs can be applied to oxygenated fuels
- Details of oxygenated fuel combustion are quite different!

High-Pressure Kinetic Mechanisms for Hydrogen and Hydrogen Syngas

1st International Workshop on Flame Chemistry
Warsaw, Poland
July 28, 2012

Michael P. Burke

Chemical Sciences and Engineering Division, Argonne National Laboratory

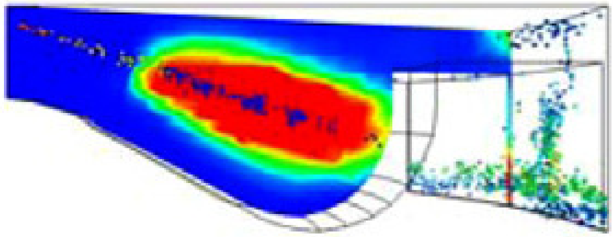
Frederick L. Dryer

Department of Mechanical and Aerospace Engineering, Princeton University

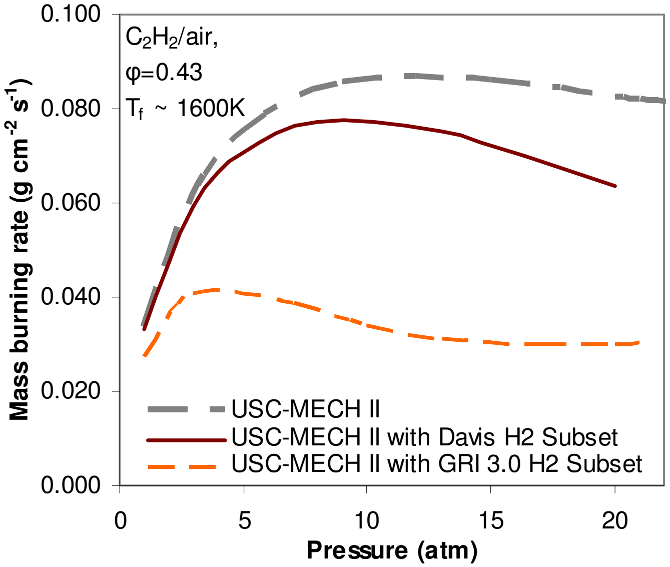
Other collaborators: Yiguang Ju, Marcos Chaos, Jeffrey Santner, Francis M. Haas
Stephen Klippenstein, Lawrence Harding

Motivation

- Growing interest in computational engine design/testing
  - Fluid mechanics and kinetics sub-models
- H_2 and H_2/CO
  - Synthesis gas ($H_2/CO/H_2O/CO_2$) from coal/biomass gasification
  - Core sub-model for all fuels
- Advanced engine technologies → High *P*, low T_f
  - Modeling difficulties for flames



(Shi & Reitz 2010)



(Burke et al. 2011)

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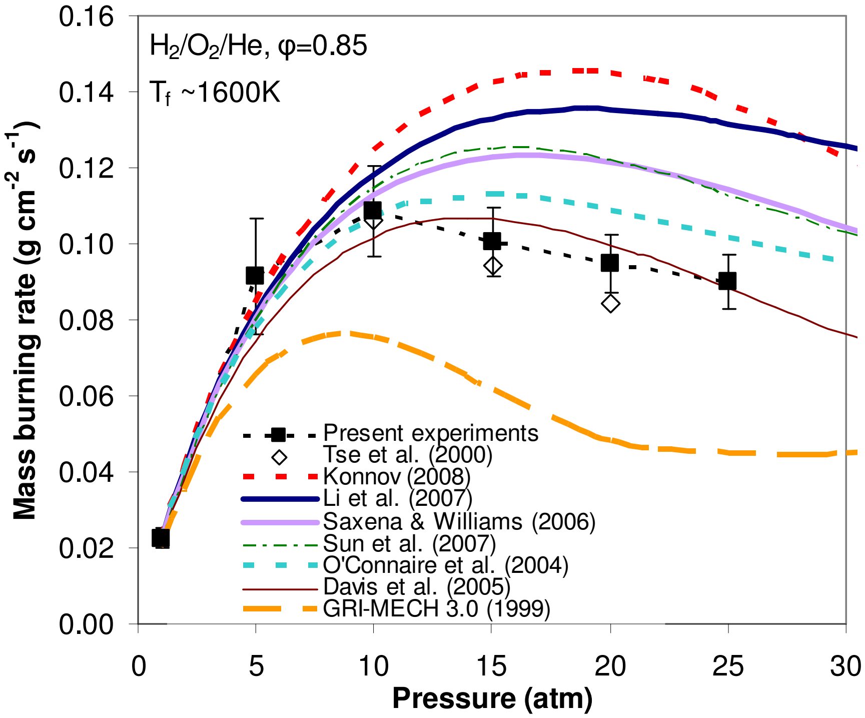
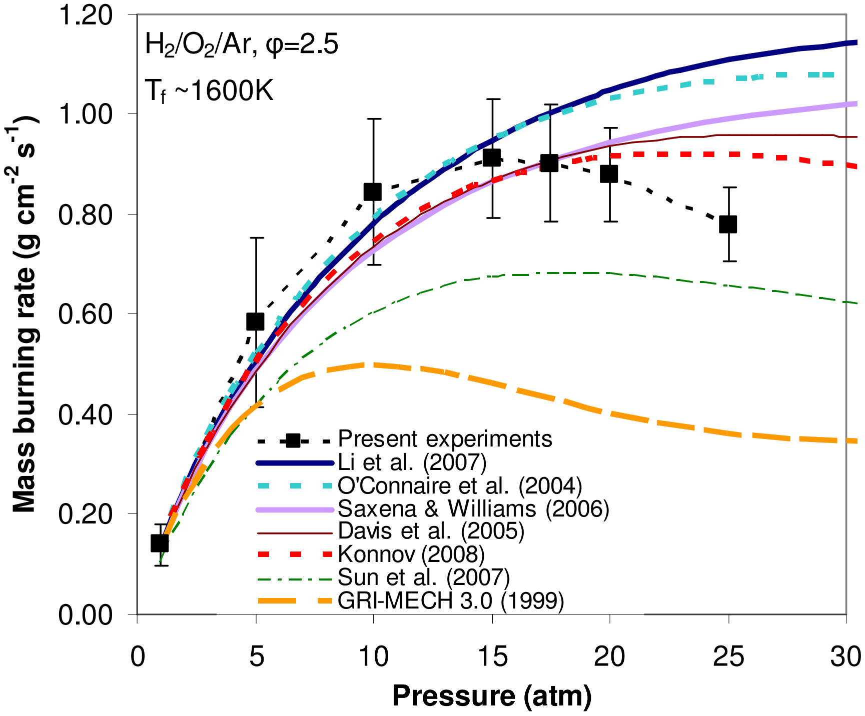
1. Y. Shi, R.D. Reitz, Fuel 89 (2010) 3416–3430.
2. M.P. Burke, M. Chaos, F.L. Dryer, Y. Ju, Combustion and Flame 157 (2010) 618-631.
3. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

Difficulty in predicting high-pressure flames





- Large variations among models
- None of the models capture pressure dependence across all conditions

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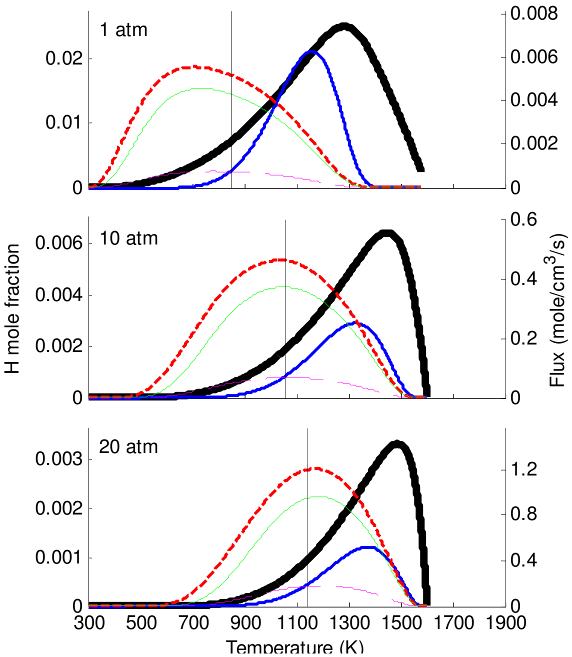
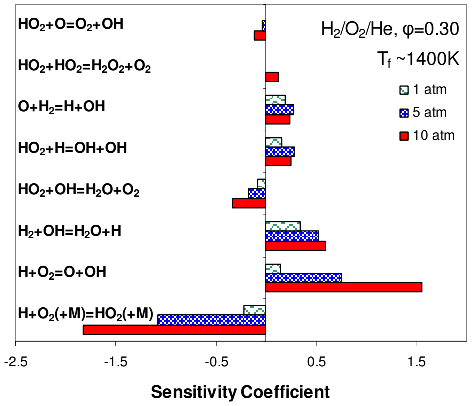
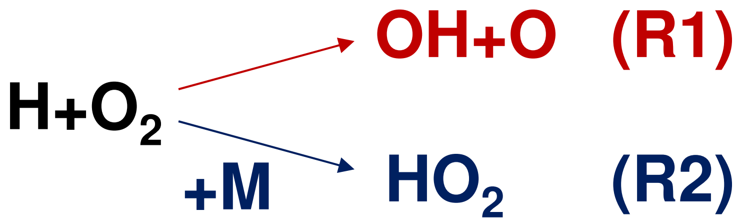
1. M.P. Burke, M. Chaos, F.L. Dryer, Y. Ju, *Combustion and Flame* 157 (2010) 618-631.
2. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

What controls high-*P*/low-T_f flames?







$H+O_2$ → **OH+O (R1)**

+M → **HO_2 (R2)**

increasing *P*

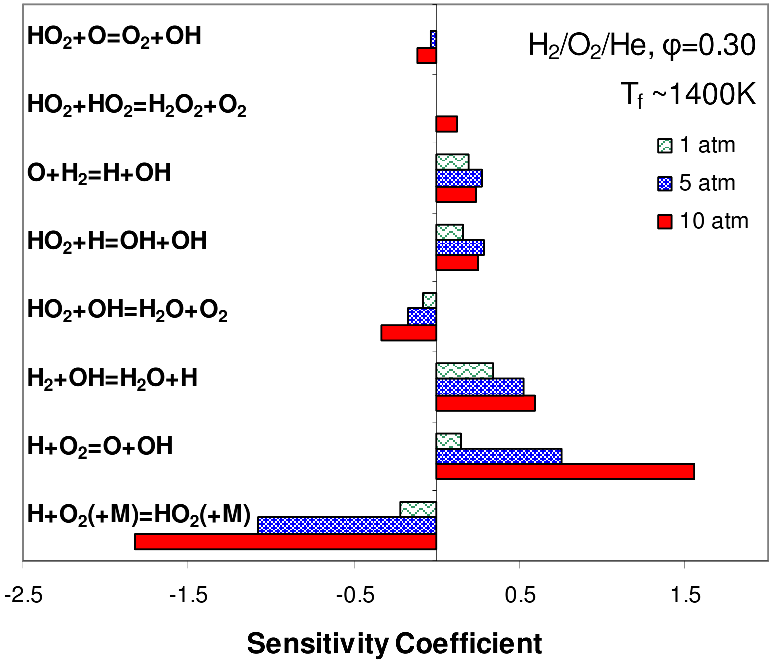
- More HO_2
  - → *more HO_2+radical flux*
- Flame zone shifts
  - → *peak sensitivity at higher T's*
  - → *collision efficiencies of products*
- More R1/R2 competition
  - → *amplified sensitivity*

(Situation similar for H_2/CO)

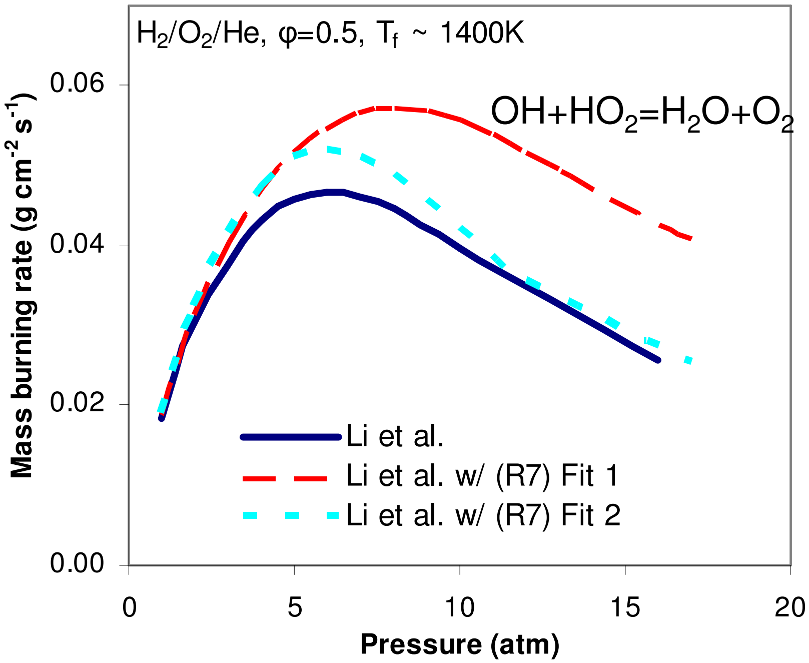
---

1. M.P. Burke, M. Chaos, F.L. Dryer, Y. Ju, *Combustion and Flame* 157 (2010) 618-631.
2. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

Complexity of the modeling problem



- Uncertainty in all reactions of 10% →burning rate uncertainty of 30%
- Realistic accuracy improvements for *elementary reactions* will not yield typical expected accuracies for *global behavior*
- Optimization against global targets necessary



- Functional temperature dependence of OH+HO_2=H_2O+O_2 highly disputed/ unknown
- Parameter optimization techniques don't work if the *functional dependence* is not known

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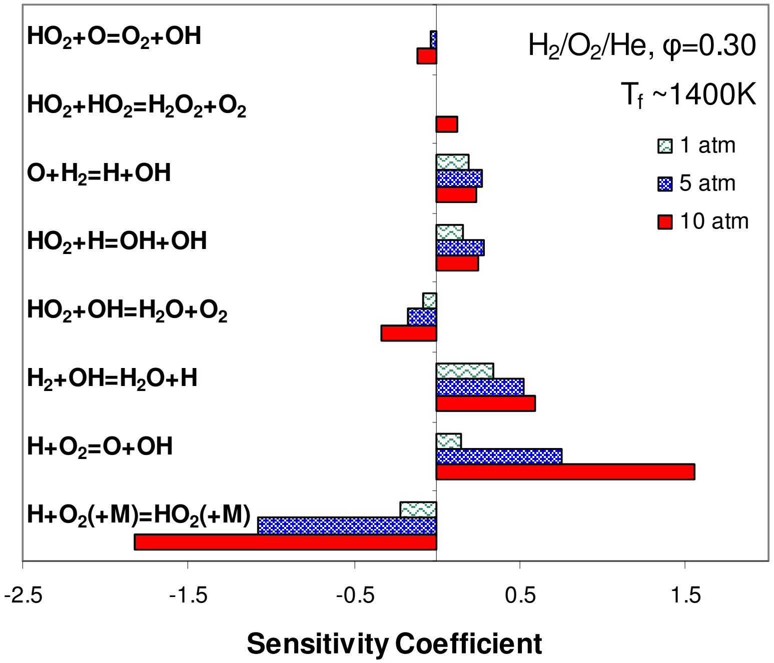
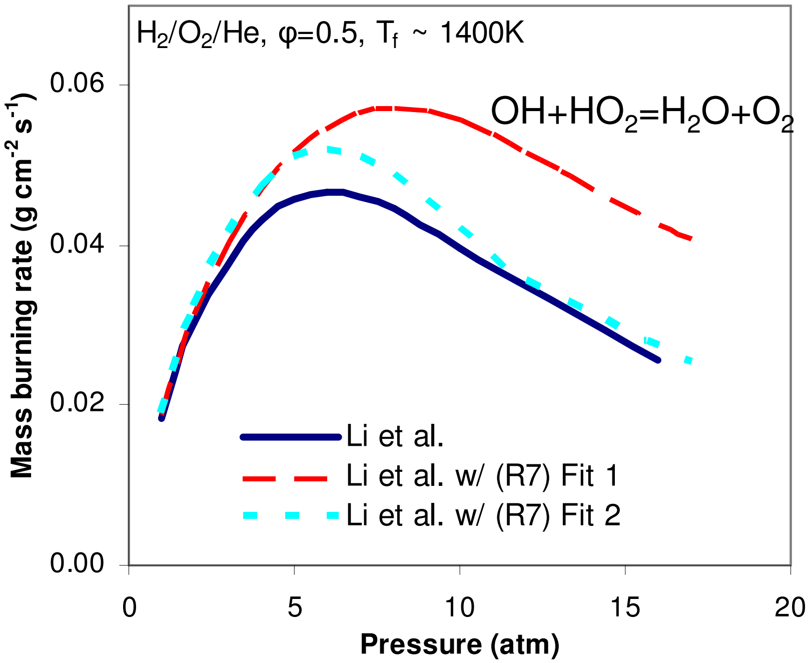
1. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

Complexity of the modeling problem





- A rigorous modeling solution will likely require ***both***:
  - Empirical adjustments to rate constants
  - Improved fundamental understanding of select processes
- Neither alone appears sufficient to solve the problem.

---

1. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

Updated kinetic-transport models

- H_2: Hong et al. (2011) and Burke et al. (2012)*
    - HO_2 formation/consumption
        - $H+O_2(+M) = HO_2(+M)$
        - HO_2+radical reactions
    - H_2O_2 reactions
    - … among others

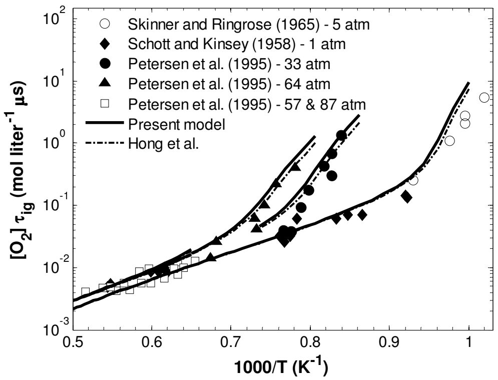
- CO: Haas et al. (2012)
    - $CO + OH = CO_2 + H$, $CO + HO_2 = CO_2 + OH$
    - HCO chemistry

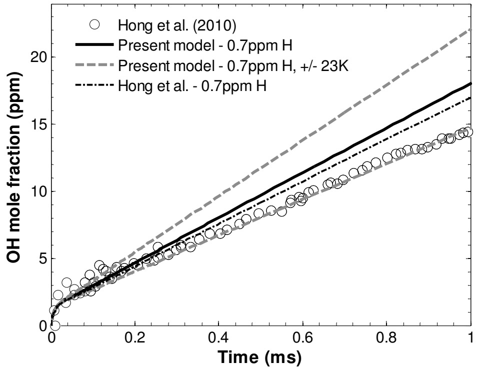
***** *Uncertainties remained: adjustments of rate parameters to improve predictions*

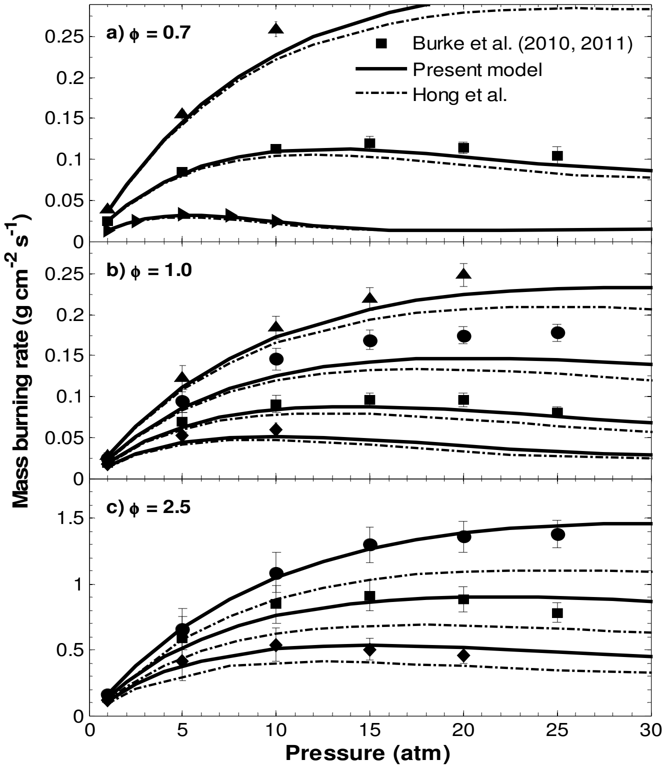
---

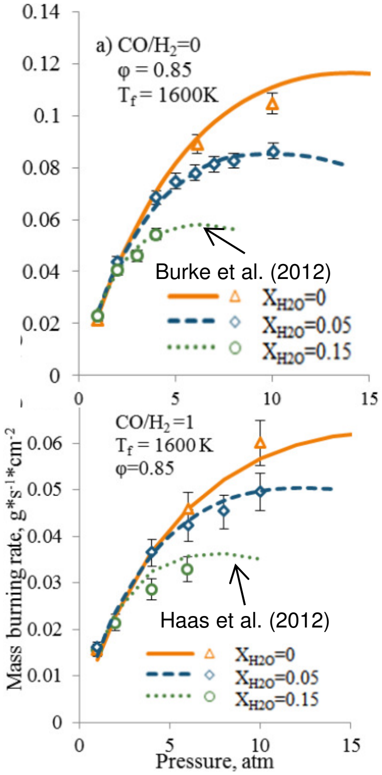
1. Z. Hong, D.F. Davidson, R.K. Hanson, *Combust. Flame* 158 (2011) 633–644.
2. M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, *Int. J. Chem. Kinet.* 44 (2012) 444-474.
3. F.M. Haas, S. Vranckx, M. Chaos, R.X. Fernandes, F.L. Dryer (2012) in preparation.

Model performance









(Santer et al. 2012, 5E01 on Friday)

- Hong/Burke perform similarly well against most targets
- Largest differences in flames
  - Burke et al. – within 20%, Hong et al. – within 40%
- Parameter adjustments not unique → uncertainties remain!

---

1. Z. Hong, D.F. Davidson, R.K. Hanson, *Combust. Flame* 158 (2011) 633–644.
2. M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, *Int. J. Chem. Kinet.* 44 (2012) 444-474.
3. F.M. Haas, S. Vranckx, M. Chaos, R.X. Fernandes, F.L. Dryer (2012) in preparation.
4. J. Santner, F.L. Dryer, Y. Ju, *Proc. Combust. Inst.* (2012) in press, oral presentation : 5E01 on Friday.

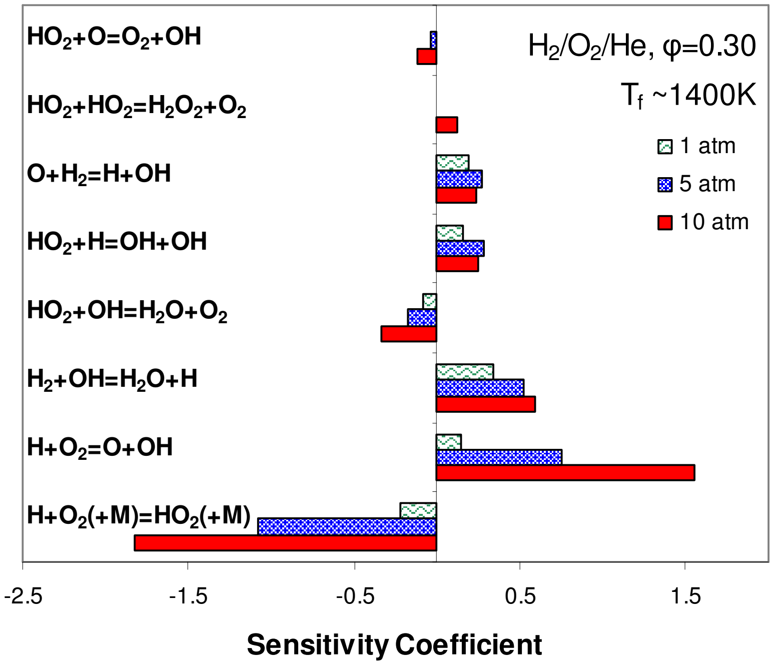
Uncertainties remaining in 2012 (for flames)

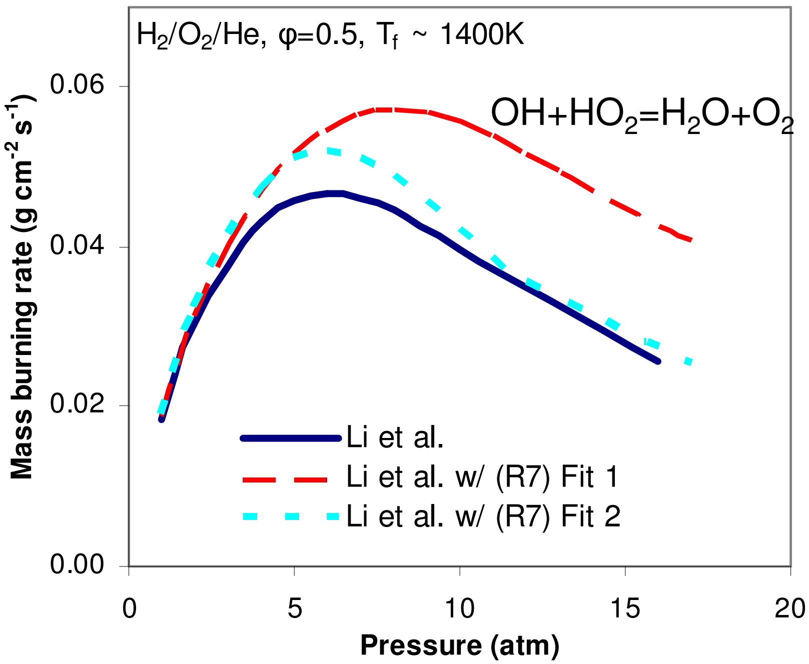
- Parametric uncertainties
  - HO_2 + X reactions
    - $HO_2 + H = OH + OH$
      $H_2 + O_2$
      $H_2O + O$
    - ***$HO_2 + OH = H_2O + O_2$***
    - $HO_2 + HO_2 = H_2O_2 + O_2$
  - $H + O_2 (+M) = HO_2 (+M)$
    - Pressure dependence
    - 3rd body efficiencies for H_2O and *CO_2*
  - $CO + O + M = CO_2 + M$
- Model assumptions
  - Nonlinear mixture rules

---

1. M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, *Int. J. Chem. Kinet.* 44 (2012) 444-474.
2. F.M. Haas, S. Vranckx, M. Chaos, R.X. Fernandes, F.L. Dryer (2012) in preparation.
3. P. Saxena, F.A. Williams, 7th US National Combustion Meeting, Atlanta, GA , 2011.

Recall the complexity of the modeling problem and uncertainties in $OH+HO_2 = H_2O+O_2$





- A rigorous modeling solution will likely require ***both***:
  - Empirical adjustments to rate constants
  - Improved fundamental understanding of select processes
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---

1. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

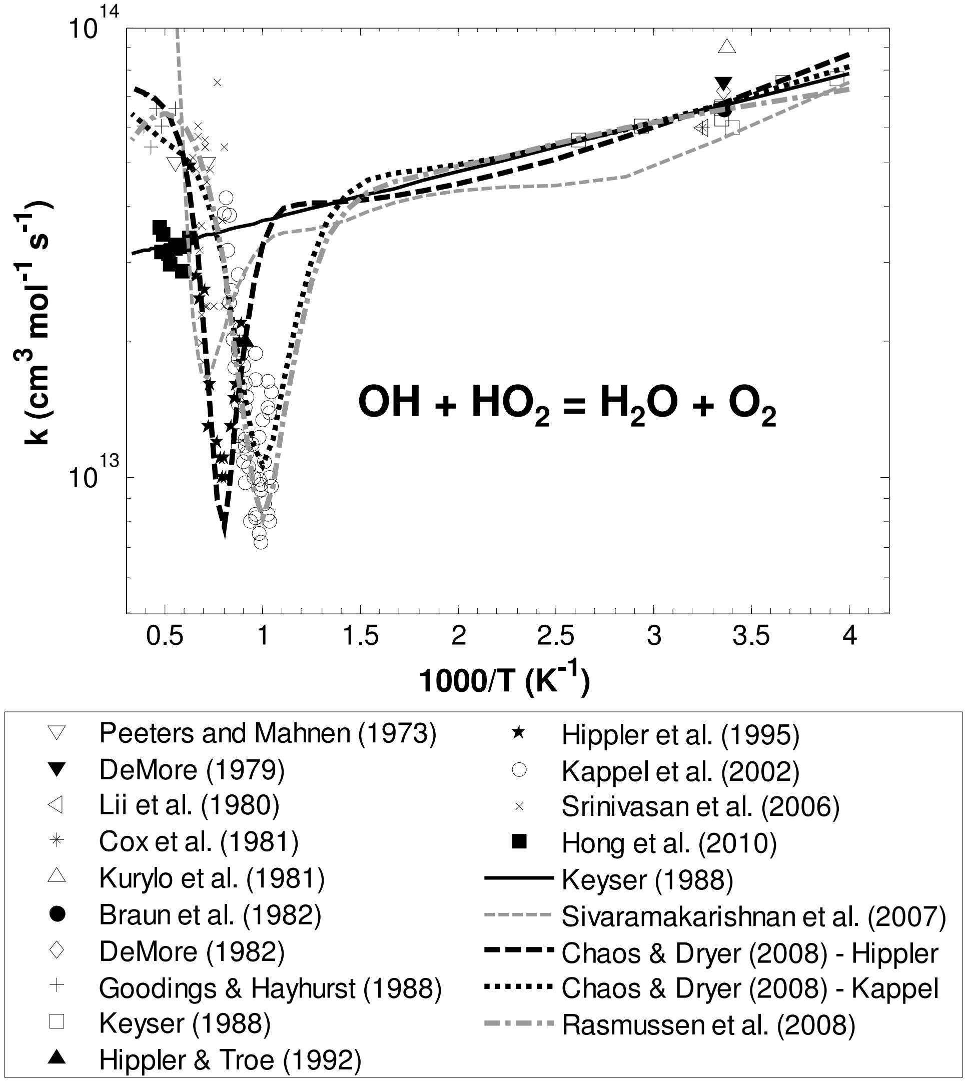
Modeling strategies

- **Current kinetic models: sets of rate parameters**
  - Hierarchical, comprehensive modeling
    - Westbrook & Dryer (1984)
  - Optimization and Uncertainty Quantification
    - Frenklach (1984), Frenklach,Wang,Rabinowitz (1992):Solution-mapping + optimization of *A*-factors
    - Frenklach et al. (2004), Sheen & Wang (2009): Uncertainty Quantification of *A*-factors
    - Turányi et al. (2012), Sheen et al. (2012): Uncertainty quantification of A-n-E_a
  - Require massive amounts of data to constrain full *T*/*P*/*M*-dependence of all *k*'s
    - Extrapolation outside the dataset very challenging
- Direct incorporation of theory useful
  - Replaces fitting formulas with physical theories
  - Common for extrapolation of data for a single reaction
  - Imposes constraints spanning all *T*/*P*/*M*
- ***Multi-scale models: sets of molecular parameters***
  - Optimal use of information from *ab initio* calculations, *k* measurements, combustion measurements
  - Theory *fills in the gaps* across all *T*/*P*/*M*

---

1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

$OH + HO_2 = H_2O + O_2$



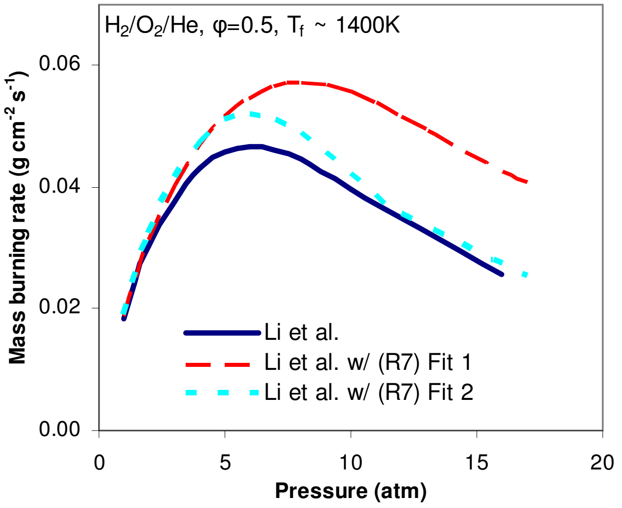
(R1) $H_2O_2(+M) = OH+OH(+M)$

(R2) $H_2O_2+OH = HO_2+H_2O$

(R3) $HO_2+HO_2 = H_2O_2+O_2$

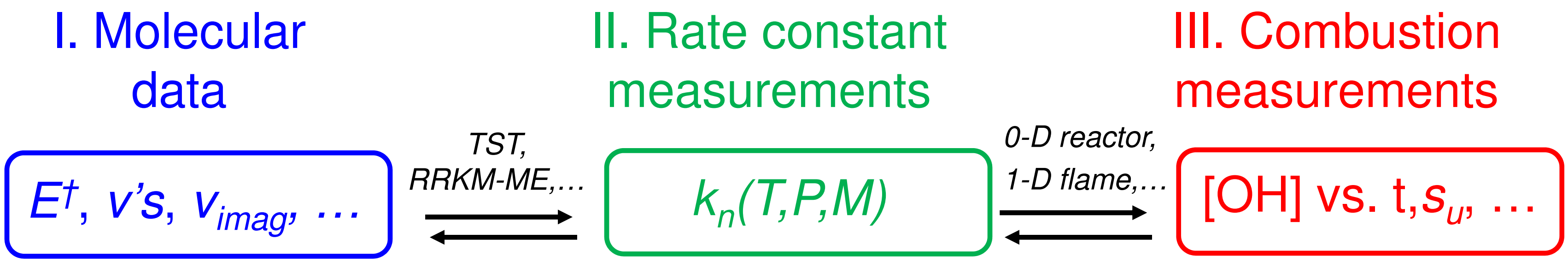
(R4) $HO_2+OH = H_2O+O_2$

(R5) $OH+OH = O+H_2O$



Multi-scale informatics

set of molecular parameters **informed by data across all scales**



I. Molecular data

II. Rate constant measurements

III. Combustion measurements

$E^\dagger$, ν's, ν_{imag}, … $\xrightarrow[\longleftarrow]{\text{TST, RRKM-ME,…}}$ $k_n(T,P,M)$ $\xrightarrow[\longleftarrow]{\text{0-D reactor, 1-D flame,…}}$ [OH] vs. t, s_u, …

Mathematical implementation

- Local "surrogate model"
- Least-squares error minimization
- Iterated until converged

X = Optimization parameters:

Molecular parameters + experimental conditions

$E^\dagger$, ν's, ν_{imag}, … + T, P, $[M_i]$,…

$$F_i(X_j) = Y_{t,i} \pm Z_i$$

(I) + (IV) $\Longrightarrow$ $S_{ij} = \delta_{ij}$

(II) $\longrightarrow$ $S_{ij} = \dfrac{\partial \ln k_{p,n}(T_i, P_i, M_i)}{\partial X_j}$

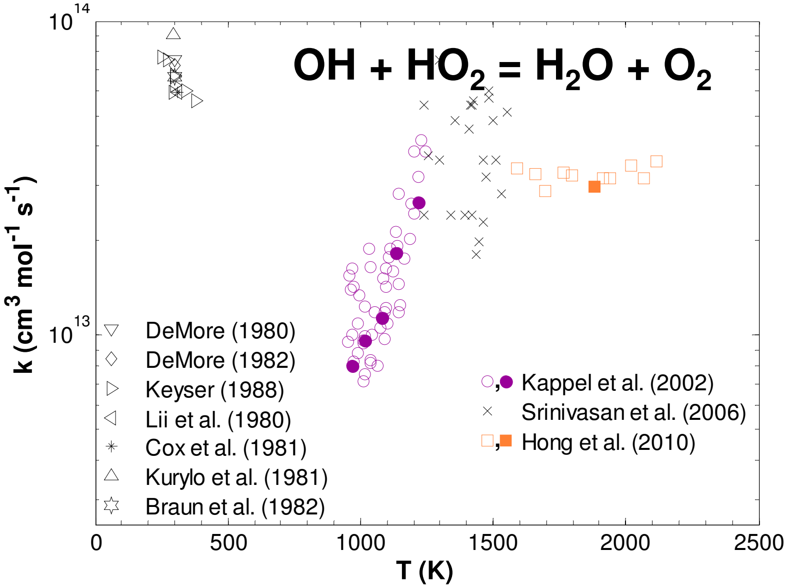
(III) $\rightarrow$ $S_{ij} = \sum_n \dfrac{\partial F_i}{\partial \ln k_{p,n}(T_i, P_i, M_i)} \dfrac{\partial \ln k_{p,n}(T_i, P_i, M_i)}{\partial X_j}$

$$\sum_j S_{ij}(X_j - \tilde{X}_j) = Y_i \pm Z_i \longrightarrow \boxed{X_{j,opt} \text{ and } C_X}$$

Implementation for H_2O_2 system

Optimization variables

$H_2O_2(+M) = OH+OH(+M)$	$A'_{(1)}, n_{(1)}, E_{(1)}$
$H_2O_2+OH = HO_2+H_2O$	$E^{\dagger}_{(2)}$, $\nu'_{all(2)}$, $\nu'_{tr(2)}$, $\nu'_{ss(2)}$, $\nu'_{imag(2)}$, $E_{w(2)}$, η'_{H2O2}, $\eta'_{TS(2)}$
$HO_2+HO_2 = H_2O_2+O_2$	$E^{\dagger}_{(3)}$, $\nu'_{all(3)}$, $\nu'_{tr(3)}$, $\nu'_{ss(3)}$, $\nu'_{imag(3)}$, $E_{w(3)}$, $\eta'_{TS(3)}$
$HO_2+OH = H_2O+O_2$	$E^{\dagger}_{(4g)}$, $\nu'_{all(4)}$, $\nu'_{tr(4g)}$, $\nu'_{ss(4g)}$, $\nu'_{imag(4g)}$, $E_{w(4g)}$, $\eta'_{TS(4g)}$
	$E^{\dagger}_{(4e)}$, $\nu'_{TS(4e)}$, $\nu'_{tr(4e)}$, $\nu'_{ss(4e)}$, $\eta'_{TS(4e)}$, $f'_{VRCTST,c(4)}$
$OH+OH = O+H_2O$	$E^{\dagger}_{(5g)}$, $\nu'_{all(5)}$, $\nu'_{tr(5g)}$, $\nu'_{ss(5g)}$, $\nu'_{imag(5g)}$, $E_{w(5g)}$
	$E^{\dagger}_{(5e)}$, $\nu'_{TS(5e)}$, $\nu'_{tr(5e)}$, $\nu'_{ss(5e)}$
Shock-heated $H_2O_2/H_2O/O_2/Ar$	T'_i, P'_i, $M'_{H2O2,o,i}$, $M'_{H2O,o,i}$, $M'_{O2,o,i}$
Shock-heated $H_2O/O_2/Ar$	T'_i, P'_i, $M'_{H2O,o,i}$, $M'_{O2,o,i}$, $M'_{H,o,i}$
Shock-heated H_2O_2/Ar	T'_i, P'_i, $M'_{H2O2,o,i}$, $\sigma'_{1,H2O2}$, $\sigma'_{2,H2O2}$, $\sigma'_{1,HO2}$, $\sigma'_{2,HO2}$



Optimization Targets

I. Molecular data:

ab initio calculations (Klippenstein/Harding)

II. Rate constant measurements:

see paper

III. Combustion measurements:

OH(t), H_2O(t)	*Shock-heated H_2O_2/Ar (Hong et al. 2009,2010)*
OH(t)	*Shock-heated H_2O/O_2/Ar (Hong et al. 2010)*
abs_{215nm}(t)	*Shock-heated H_2O_2/Ar (Kappel et al. 2002)*

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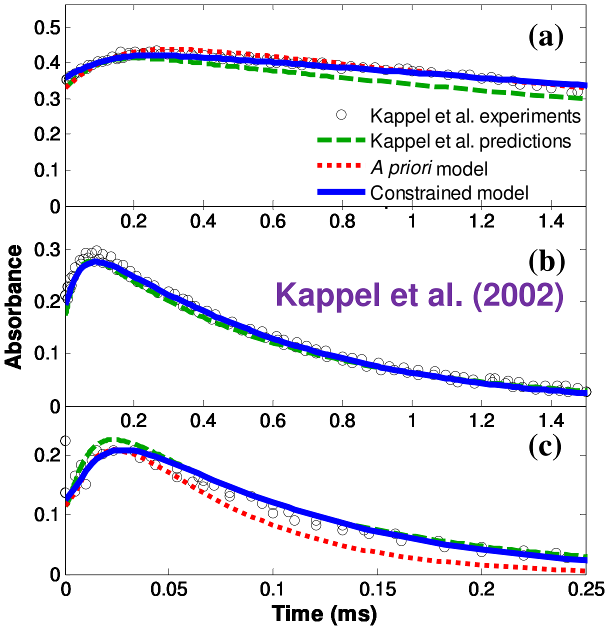
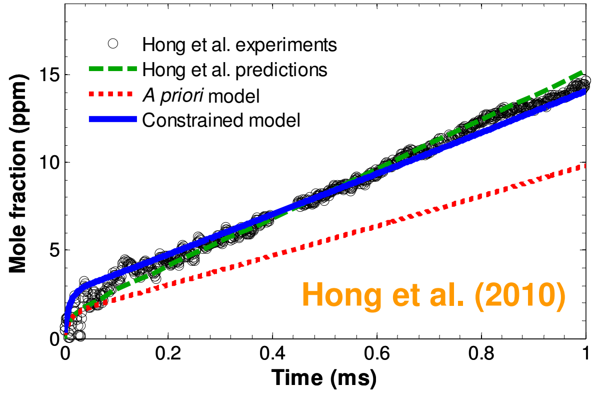
1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

Different interpretations for $OH+HO_2$



Much weaker *T*-dependence

(Secondary reactions)



Lower magnitude

(Arbitrary H atom doping)

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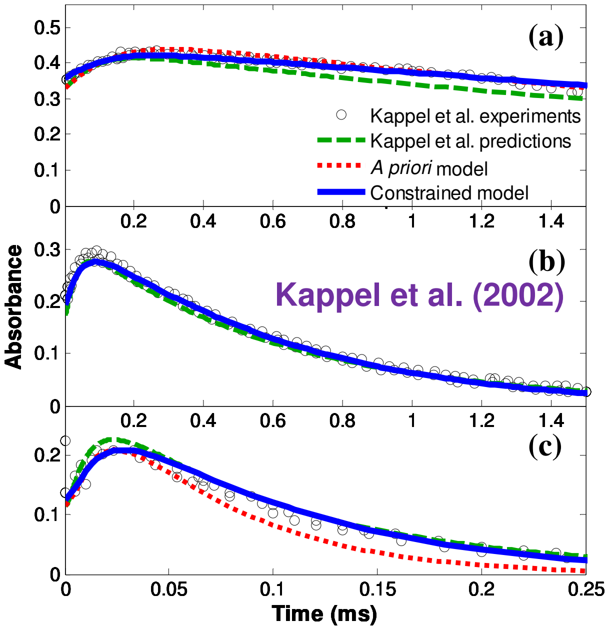
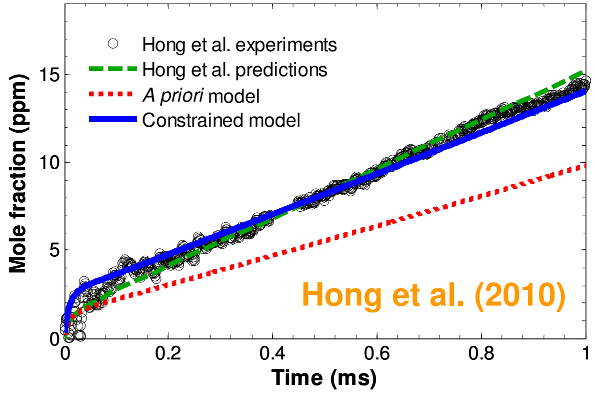
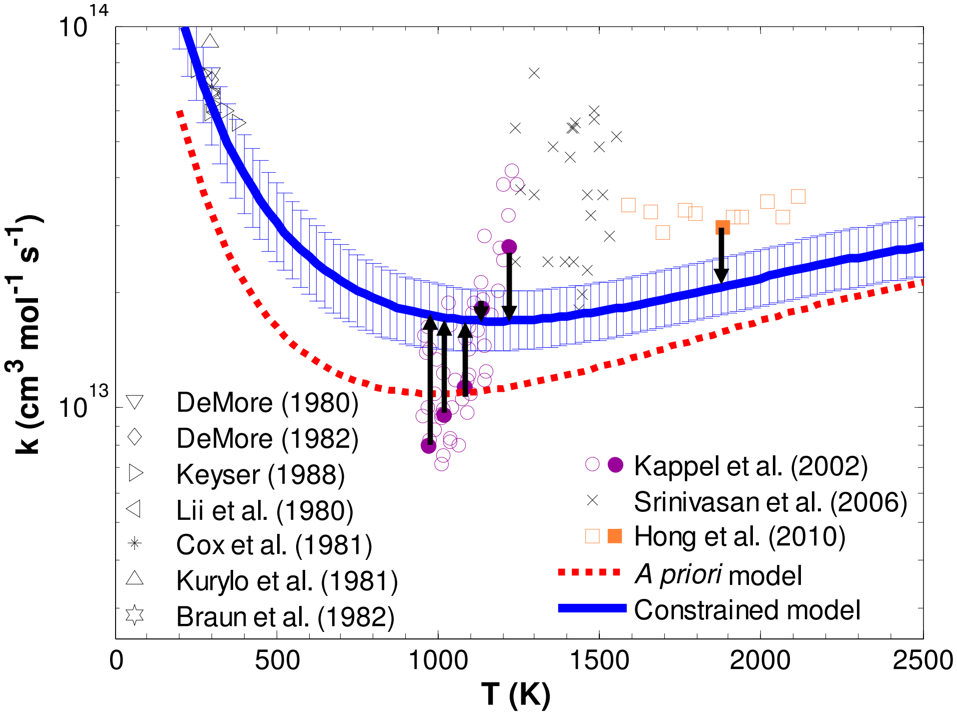
1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

Consistent description of $OH+HO_2 = H_2O+O_2$







- Single description consistent with:
  1. *Ab initio* calculations
  2. Low-T k measurements
  3. High-T raw global data
- Milder T-dependence
  - Minimum near 1200 K

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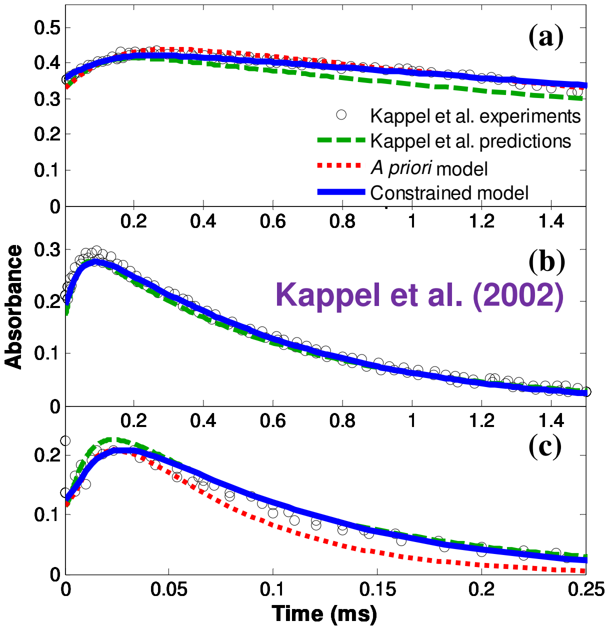
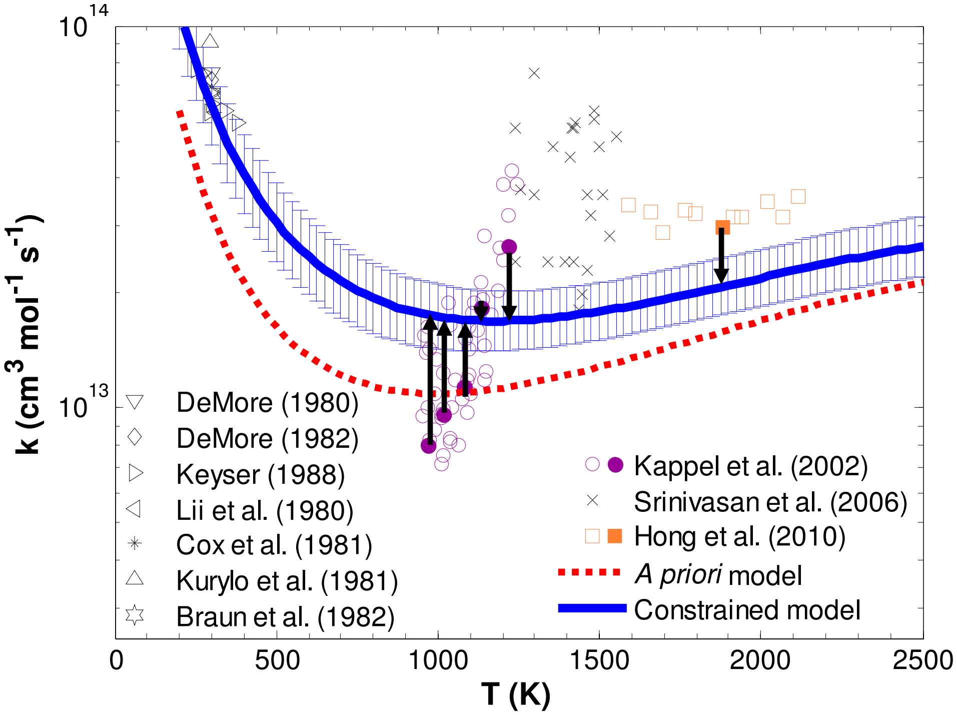
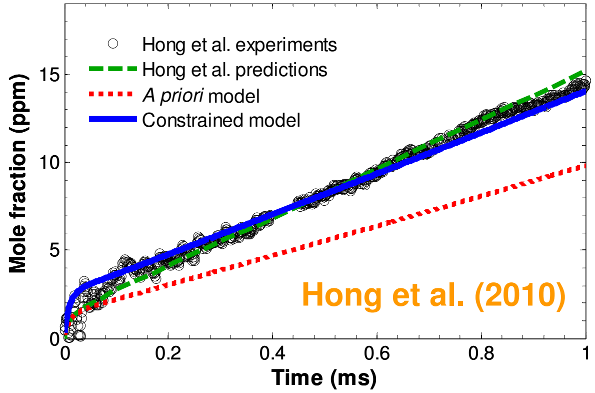
1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

Consistent description of $OH+HO_2 = H_2O+O_2$







- *Simultaneous weighting* of diverse data types
  - Theory guides experimental interpretations
- Raw data and careful documentation extremely powerful

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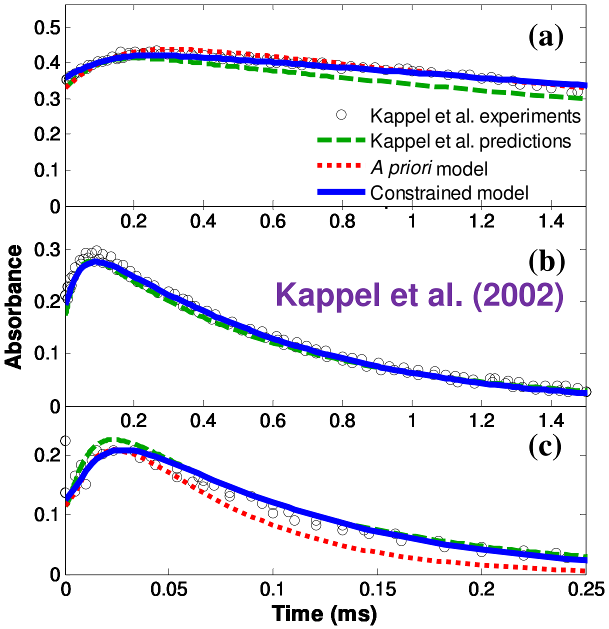
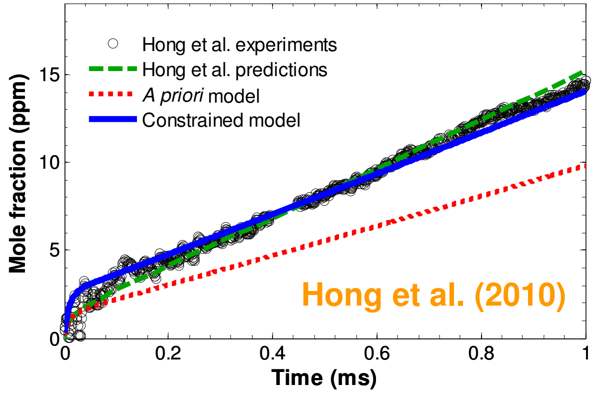
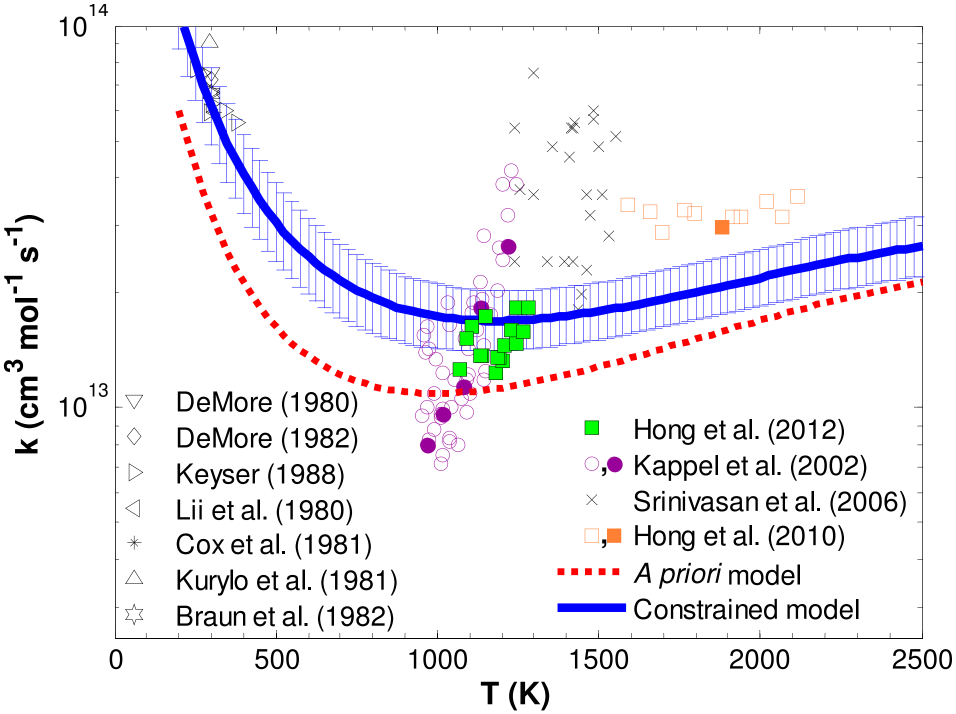
1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

Consistent description of $OH+HO_2 = H_2O+O_2$







Z. Hong, K.-Y. Lam, R. Sur, S. Wang, D.F. Davidson, R.K. Hanson

"On the rate constants of $OH + HO_2$ and $HO_2 + HO_2$: A comprehensive study of H_2O_2 thermal decomposition using multi-species laser absorption."

Combustion Symposium: 5D11

M.P. Burke, S.J. Klippenstein, L.B. Harding

"A quantitative explanation for the *apparent* anomalous temperature dependence of $OH + HO_2 = H_2O + O_2$ through multi-scale modeling."

Combustion Symposium: 4D09

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1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.
2. Z. Hong, K.-Y. Lam, R. Sur, S. Wang, D.F. Davidson, R.K. Hanson, *Proc Combust Inst* (2012) in press.

Conclusions

- High-pressure syngas flames
  - Emphasize HO_2 pathways + collision efficiencies of CO_2/H_2O
  - Inherently difficult to model
- Rigorous modeling solutions
  - Empirical adjustments based on global targets
  - Improved fundamental characterization
- Uncertainties remain in both 1) model parameters and 2) model assumptions
- Moving forward
  - Incorporation of theory to *fill in the gaps*
  - Raw data and careful documentation
  - Characterization of non-idealities/uncertainties in experiments and theory

Acknowledgements

- This work was supported by:
  - Director's Postdoctoral Fellowship from Argonne National Laboratory (MPB)
  - U. S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357 (SJK, LBH)
  - U. S. Department of Energy, University Turbine Systems Research Program under Contract No. DE-NT0000752 (FLD,YJ)
  - U.S. Department of Energy, Office of Basic Energy Sciences, Energy Frontier Research Center under Contract No. DE-SC0001198 (FLD,YJ)

Princeton University

Mechanical & Aerospace Engineering Department

Thank you.

Questions?

End

Determination of the joint uncertainty domain of rate parameters:

The case study of hydrogen combustion

T. Turányi, T. Nagy, I.Gy. Zsély, T. Varga,
R. Pálvölgyi, I. Sedyó, C. Olm, H. J. Curran

Laboratory for Chemical Kinetics
Institute of Chemistry, Eötvös University (ELTE),
Budapest, Hungary

Uncertainty of rate coefficients

Definition of uncertainty factor *f*:

$$f(T) = \log_{10}\left(k^{0}(T)/k^{\min}(T)\right) = \log_{10}\left(k^{\max}(T)/k^{0}(T)\right)$$

Calculation of the variance of ln *k* from uncertainty factor *f*
(assuming 3σ deviation between ln k^0 and ln $k^{\max}$):

$$\sigma(\ln k) = \frac{\ln 10}{3} f$$

The databases of evaluated combustion kinetic rate parameters
e.g. Baulch *et al.*, 2005

- recommended temperature independent (constant) uncertainty
  (usually selected from values $f = 0.1$, 0.3, 0.5, 0.7, and 1.0)

OR

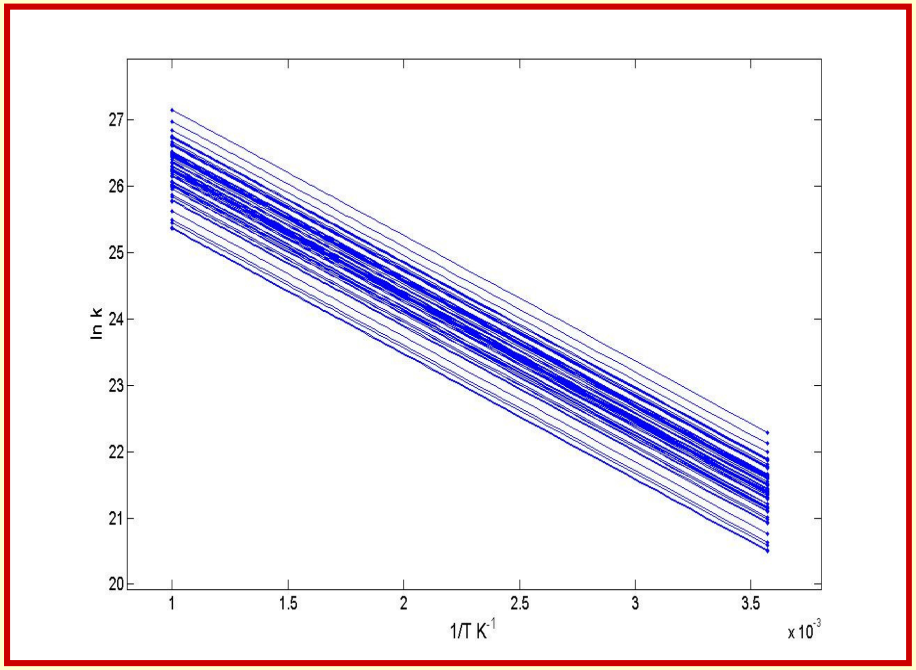
- uncertainty is defined at some temperatures (or temperature intervals)

Uncertainty parameter *f* in the databases

Features of uncertainty factor *f*:

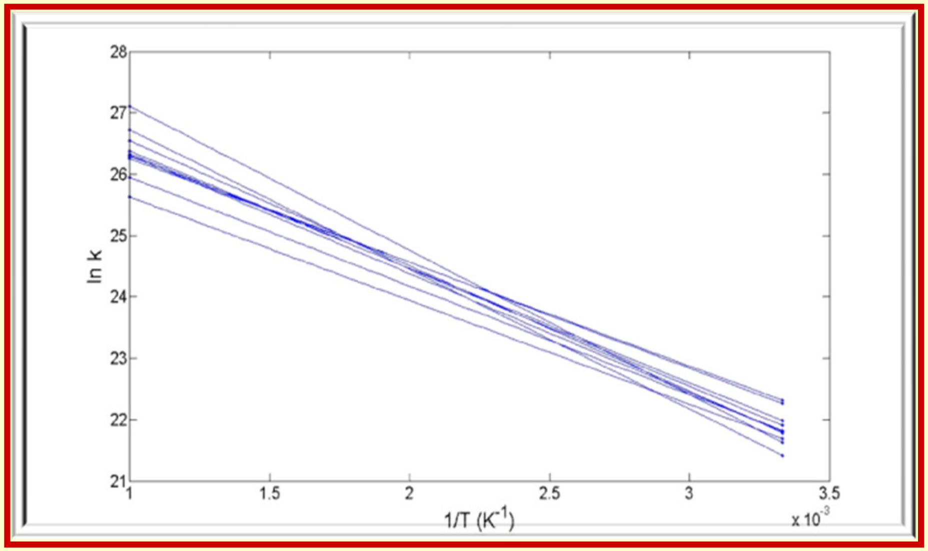
- widely used in the data collections / data evaluations (Warnatz, Tsang, Konnov, Baulch, NIST)
- available for most reactions
- some uncertainty analysis works have used it
- important input information in the mechanism optimization works of Frenklach *et al.* and Wang *et al.*
- no statistical background, subjective assessment
- Usually reflects a wider uncertainty than the quoted experimental uncertainty of the "best" measurement
- temperature dependence:
  - quoted to be temperature independent (50%)
  - defined at several (2-3) temperatures (50%)

Arrhenius plot (ln *k* vs. 1/*T*) with uncertain parameter *A*:



uncertainty of
⇒ the rate coefficient
is independent
of temperature

Arrhenius plot (ln *k* vs. 1/*T*) with uncertain parameters *A* and *E*:



uncertainty of
⇒ the rate coefficient
depends
on temperature

extended Arrhenius expression: $\boxed{k(T) = AT^n \exp(-E/RT)}$

linearized form: $\boxed{\underbrace{\ln\{k(T)\}}_{\kappa(\theta)} = \underbrace{\ln\{A\}}_{\alpha} + \underbrace{n}_{n} \cdot \ln\underbrace{\{T\}}_{\theta} - \underbrace{\{E/R\}}_{\varepsilon} \cdot \underbrace{\{T\}}_{\theta}^{-1}}$

- Matrix-vector form of the linearized Arrhenius equation:

$$\boxed{\mathbf{p}^{\mathrm{T}} := [\alpha \;\; n \;\; \varepsilon]} \qquad \boxed{\boldsymbol{\theta}^{\mathrm{T}} := [1 \quad \ln T \quad -T^{-1}]} \qquad \boxed{\kappa(\theta) = \mathbf{p}^{\mathrm{T}}\boldsymbol{\theta}}$$

- The covariance matrix of the Arrhenius parameters and its relation to the uncertainty of the rate coefficient:

$$\boxed{\boldsymbol{\Sigma}_{\mathbf{p}} = \overline{(\mathbf{p}-\overline{\mathbf{p}})(\mathbf{p}-\overline{\mathbf{p}})^{\mathrm{T}}} = \begin{bmatrix} \sigma_\alpha^2 & r_{\alpha n}\sigma_\alpha\sigma_n & r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon \\ r_{\alpha n}\sigma_\alpha\sigma_n & \sigma_n^2 & r_{n\varepsilon}\sigma_n\sigma_\varepsilon \\ r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon & r_{n\varepsilon}\sigma_n\sigma_\varepsilon & \sigma_\varepsilon^2 \end{bmatrix}}$$

$$\boxed{\sigma_\kappa(\theta) = \sqrt{\boldsymbol{\theta}^{\mathrm{T}}\boldsymbol{\Sigma}_{\mathbf{p}}\boldsymbol{\theta}}}$$

⇒ the temperature dependent standard deviation of *k* can be calculated from a quadratic form.

Relation between the rate coefficient and the covariance matrix of the Arrhenius parameters

- For the 3-parameter Arrhenius equation

$$\boxed{\sigma_\kappa(\theta)=\sqrt{\sigma_\alpha^2+\sigma_n^2\ln^2\theta+\sigma_\varepsilon^2\theta^{-2}+2r_{\alpha n}\sigma_\alpha\sigma_n\ln\theta-2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon\theta^{-1}-2r_{n\varepsilon}\sigma_n\sigma_\varepsilon\ln\theta\cdot\theta^{-1}}}$$

- For the original (2-parameter) Arrhenius equation:

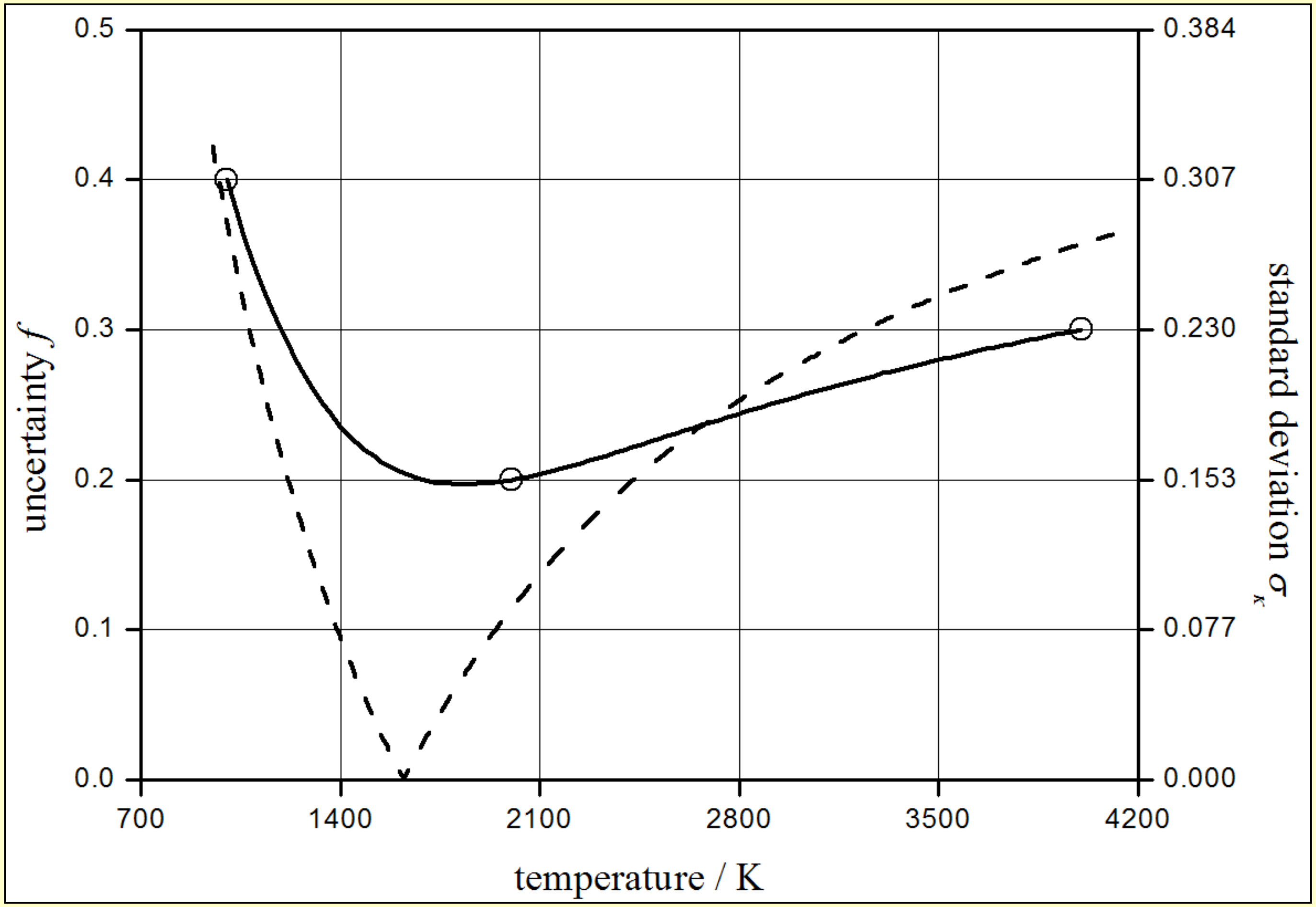
$$\boxed{\sigma_\kappa(\theta)=\sqrt{\sigma_\alpha^2+\sigma_\varepsilon^2\theta^{-2}-2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon\theta^{-1}}}$$

⇒ If the variance of *k* is known at several (at least 6) temperatures
the covariance matrix of the Arrhenius parameters can be calculated

⇒ The uncertainty limits of the Arrhenius parameters can be determined.

⇒ If ln *k* has normal distribution ⇔ the Arrhenius parameters
have joint multivariate normal distribution.

Reaction $O + N_2O \rightarrow NO + NO$ temperature dependence of the uncertainty of the rate coefficient (1000K–4000K)

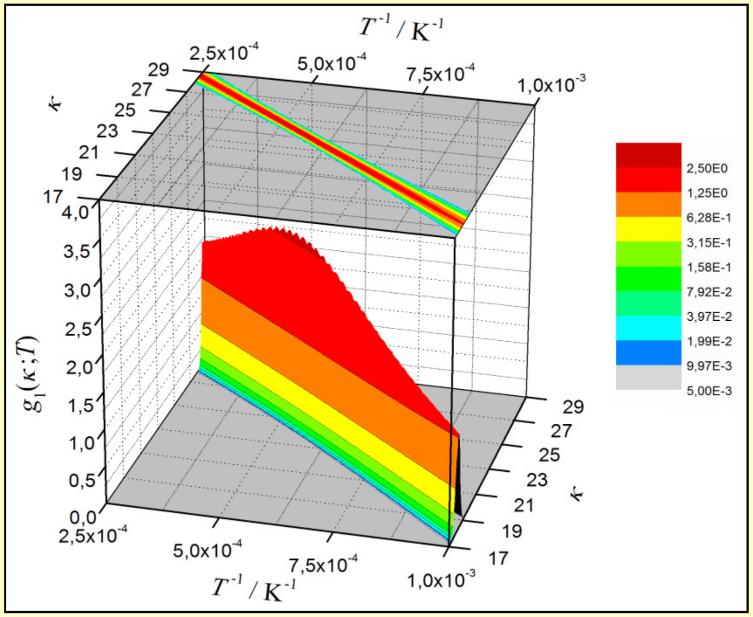


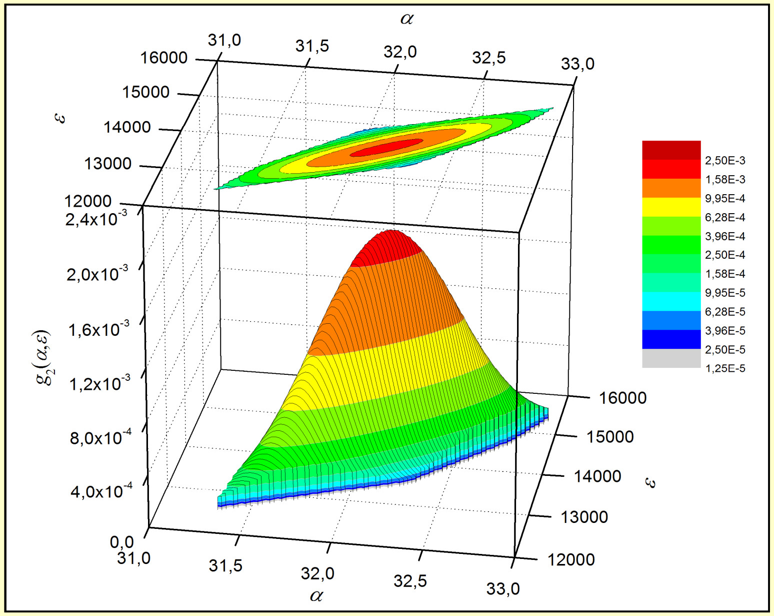
$$k(T) = A\exp(-E/RT)$$
$$\kappa(\theta) = \alpha - \varepsilon \cdot \theta^{-1}$$
$$\overline{\alpha} = 32{,}134$$
$$\overline{\varepsilon} = 13930$$

$$\sigma_{\alpha} = 0{,}355$$
$$\sigma_{\varepsilon} = 588$$
$$r_{\alpha\varepsilon} = 0{,}9045$$

Reaction O + N_2O → NO + NO

$$\sigma_\kappa(\theta)=\sqrt{\sigma_\alpha^2+\sigma_\varepsilon^2\theta^{-2}-2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon\theta^{-1}}$$





Temperature dependent
1D normal
probability density function (*pdf*)
of the rate coefficient
(1000 K – 4000 K)

Temperature independent
multivariate joint normal
probability density function (*pdf*)
of the Arrhenius parameters

Estimation of the temperature dependent uncertainty

For most of the reactions the data evaluations define

- **temperature independent *f* (constant *f*(*T*) function)**

OR

- **a verbally defined *f*(*T*) function**

”*f* = 0.1 at 800 K raising to 0.2 at 2000 K ”

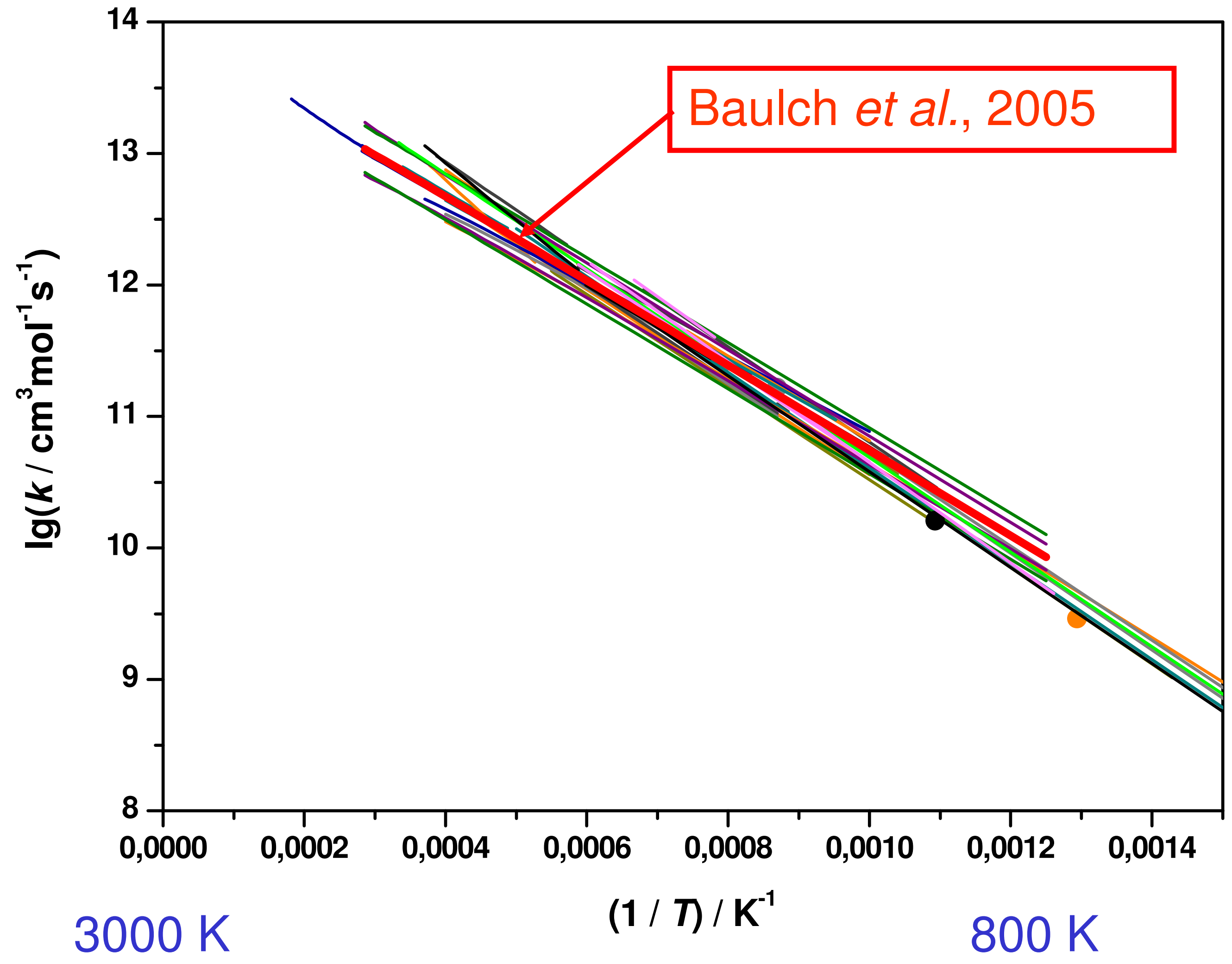
Reassessment of the *f*(*T*) functions is needed!

Example:

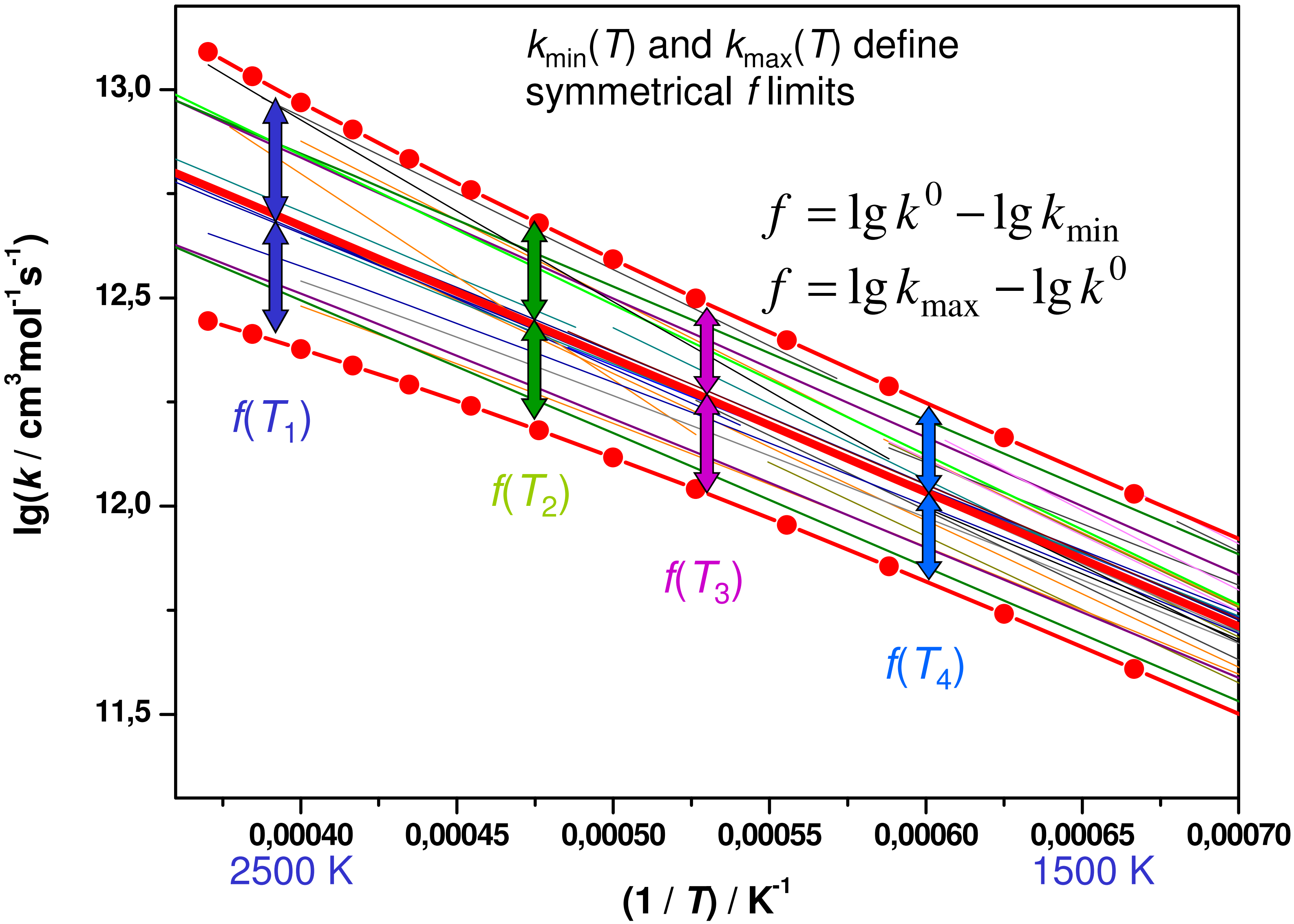
$\mathbf{H + O_2 = OH + O}$

Reaction H + O_2 → O + OH

All experimental and theoretical (TST) results from the NIST database



Definition of $k_{\min}$ and $k_{\max}$ ranges of uncertainty

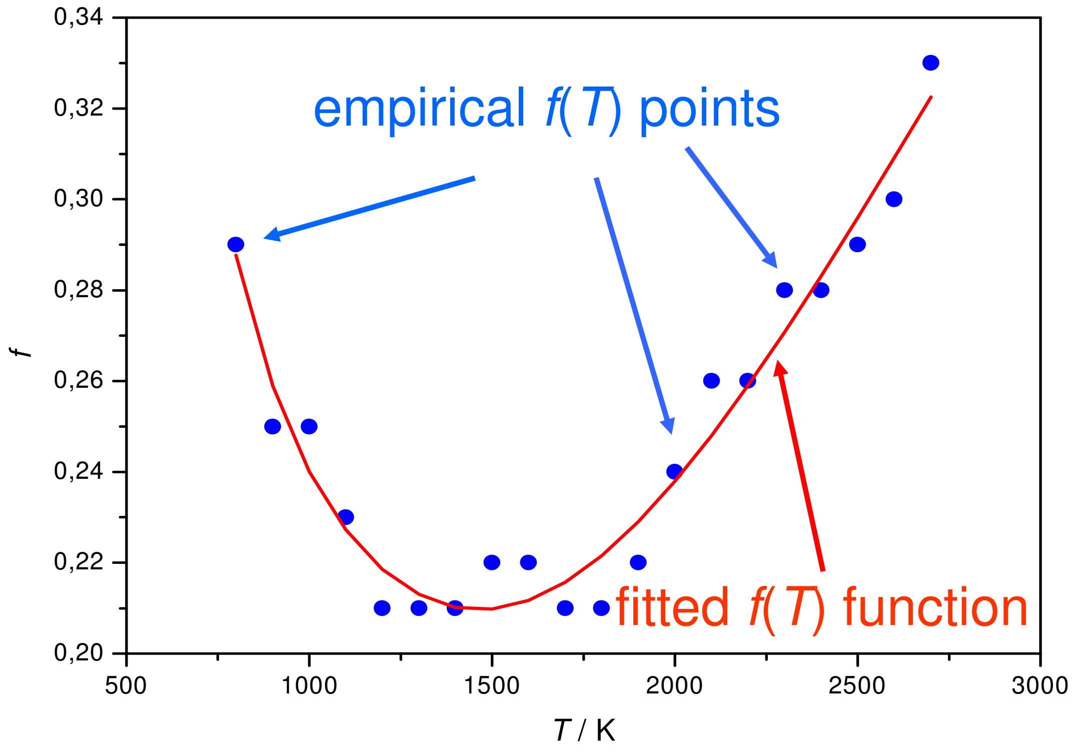


$k_{\min}(T)$ and $k_{\max}(T)$ define symmetrical f limits

$$f = \lg k^0 - \lg k_{\min}$$

$$f = \lg k_{\max} - \lg k^0$$

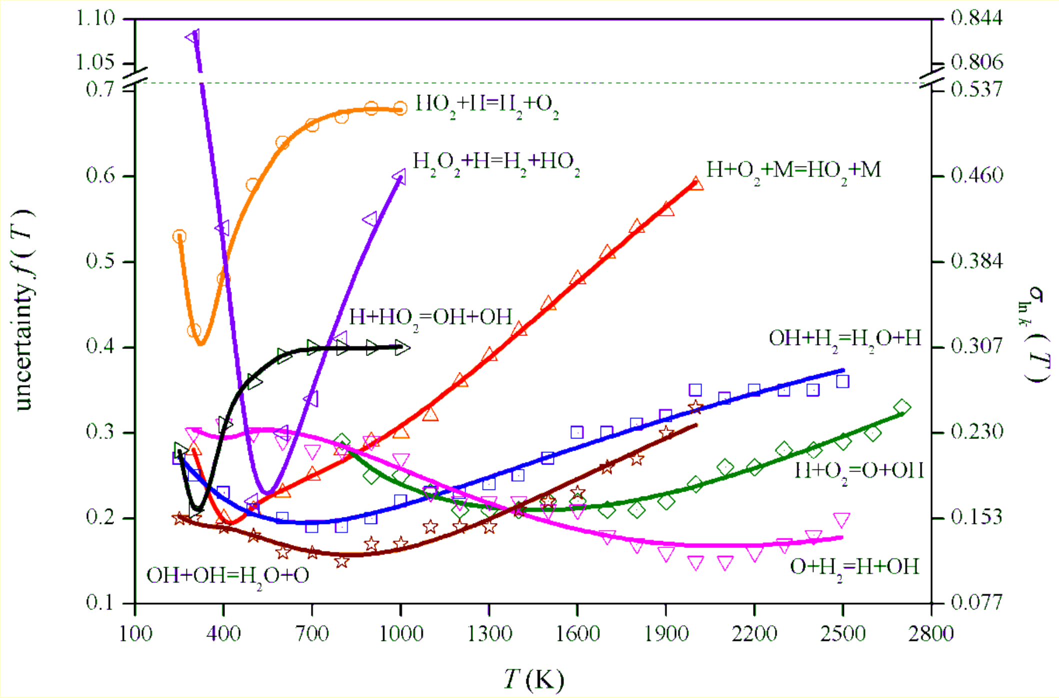
Empirical *f*(*T*) points and fitted *f*(*T*) function



$$f(T) = \frac{3}{\ln 10}\sqrt{\sigma_\alpha^2 + \sigma_\varepsilon^2 T^{-2} + \sigma_n^2 \ln^2 T - 2 r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon T^{-1} - 2 r_{\varepsilon n}\sigma_\varepsilon\sigma_n T^{-1}\ln T + 2 r_{\alpha n}\sigma_\alpha\sigma_n \ln T}$$

Nagy, T.; Turányi, T.
Uncertainty of Arrhenius parameters
Int. J. Chem. Kinet., **43**, 359-378(2011)

Temperature dependence of the uncertainty of the rate coefficients of the most important H/O reactions



The procedure above was repetead for several H/O reactions

Sedyó, I; Nagy, T; Zsély, I; Turányi, T
Uncertainty of the Arrhenius parameters of important elementary reactions of the hydrogen-oxygen system
Proceedings of the ECM, 2011

Comprehensive determination of the uncertainty of the rate parameters

Required features

1. **The determination should take into account all available information:**
   Direct measurements: determination of the rate coefficient of a single reaction step at given temperature, pressure and bath gas
   Indirect measurements: ignition delay time, laminar flame velocity, measured concentration profiles
   Theoretical calculations / estimations: uncertainty is critical

2. **Statistics based (reproducible) definition of the uncertainty**

3. **Joint uncertainty for all rate parameters:**
   Arrhenius parameters *A*, *n*, *E* for each reaction step,
   3rd body efficiencies, parameters of pressure dependence

4. **Extensions:**
   thermodynamic data: in accordance with the ATcT method
   other parameters of simulations: *e.g.* transport data

Step 1: Collection of large amount of indirect measurements

Aim: collection of all direct and indirect measurement, ever measured, related to hydrogen combustion

Reality: pre-selection was needed, many obsolate measurements (before about 1950) were not considered

- **ignition delay time measurements in shock tubes**: 796 data points in 55 data series from 17 publications
- **ignition delay time measurements in rapid compression machines (RCMs)**: 623 data points in 44 data series from one publication
- **Laminar flame velocity measurements**: 622 data points in 64 data series from 23 publications
- **concentrations measured in PSRs**: 152 data points in 9 data series from one publication
- **concentration–distance profiles in turbulent flow reactors**: 214 data points in 16 data series from one publication

Total: 2407 data points in 188 data series from 43 publications.

All experimental data were encoded in PrIMe XML data format.

PrIMe database

PrIMe (Process Informatics Model) database of Michael Frenklach:

www.primekinetics.org

Open database that contains the description of several hundred indirect combustion measurements.

Special XML data format:
defines all experimental conditions and measurement data.

We have created computer codes for

- encoding literature data OR other experimental data in PrIMe XML format
- carrying out simulations based on a PrIMe datafile (ignition in shock tube, laminar stationary flame, tubular reactor)
- calculating the deviations between the experimental and simulated data

PrIMe-format encoding of a shock tube experiment

```
<commonProperties>
    <property description="pressure behind reflected shock waves"
        label="P5" name="pressure" units="atm">
        <value>64</value>
        <uncertainty bound="plusminus" kind="relative"
        transformation="1">0.01</uncertainty>
    </property>
  <property name="initial composition">
     <component>
        <speciesLink preferredKey="H2" primeID="s00009809" />
        <amount units="mole fraction">0.0033</amount>
     </component>
     <component>
        <speciesLink preferredKey="O2" primeID="s00010295" />
        <amount units="mole fraction">0.00167</amount>
     </component>
     <component>
        <speciesLink preferredKey="Ar" primeID="s00000049" />
        <amount units="mole fraction">0.99503</amount>
      </component>
   </property>
 </commonProperties>
```

Step 2: Cross testing of mechanisms vs. data

Mechanisms:

Group 1: hydrogen combustion mechanisms

- **Ó Conaire 2004:** 10 species, 21 reactions
  Ó Conaire, M.; Curran, H. J.; Simmie, J. M.; Pitz, W. J.; Westbrook, C. K. *Int. J. Chem. Kinet.* **2004, 36, 603-622.**
- **Konnov 2008:** 10 species, 33 reactions
  Konnov, A. A. *Combust. Flame* **2008, 152, 507-528.**
- **Hong 2011:** 10 species, 31 reactions
  Hong, Z.; Davidson, D. F.; Hanson, R. K. *Combust. Flame* **2011, 158, 633-644.**
- **Burke 2012:** 11 species, 27 reactions
  Burke, M. P.; Chaos, M.; Ju, Y.; Dryer, F. L.; Klippenstein, S. J. *Int. J. Chem. Kinet.* **2012, 44, 444-474.**

Group 2: originally developed for wet CO combustion

- **Zsély 2005:** 10 species, 32 reactions
  Zsély, I. G.; Zádor, J.; Turányi, T. *Proc. Combust. Instit.* **2005, 30/1, 1273-1281.**
- **Sun 2007:** 11 species, 32 reactions
  H. Sun, S.I. Yang, G. Jomaas, C.K. Law, *Proc. Comb. Inst.* **2007, 31, 439-446.**
- **CRECK 2012:** 11 species, 21 reactions
  Frassoldati, A.; Ranzi, E.; Faravelli, T. CRECK modeling Group Hydrogen/CO mechanism version 1201.
  http://creckmodeling.chem.polimi.it/kinetic.html
- **Rasmussen 2008:** 10 species, 30 reactions
  C. L. Rasmussen; J. Hansen; P. Marshall; P. Glarborg, *Int. J. Chem. Kinet.* **2008, 40, 454-480.**
- **Keromnes 2012:** 12 species, 33 reactions
  A. Keromnes, W. K. Metcalfe, K. A. Heufer, N. Donohoe, A. K. Das, C. J. Sung, J. Herzler, C. Naumann, P. Griebel, O. Mathieu, M. C. Krejci, E. L. Petersen, W. J. Pitz, H. J. Curran, *Combust. Flame* (submitted)

Group 3: originally developed for hydrocarbon combustion

- **GRI 3.0:** 10 species, 29 reactions
  Smith, G P; Golden, D M; Frenklach, M; Moriary, N W; Eiteneer, B; Goldenberg, M; Bowman, C T; Hanson, R K; Song, S; Gardiner, W C; Lissianski, V V; Qin, Z GRI-Mech 3.0 http://www.me.berkeley.edu/gri_mech/ 23/11/2011/
- **Li 2007:** 11 species, 25 reactions
  Li, J.; Zhao, Z.; Kazakov, A.; Chaos, M.; Dryer, F. L.; Scire, J. J. J. *Int. J. Chem. Kinet.* **2007, 39, 109-136.**
- **USC 2007:** 10 species, 28 reactions
  H. Wang; X. You; A. V. Joshi; S. G. Davis; A. Laskin; F. Egolfopoulos; C. K. Law USC Mech Version II. High-Temperature Combustion Reaction Model of H_2/CO/C_1-C_4 Compounds. http://ignis.usc.edu/USC_Mech_II.htm (May 2007)
- **San Diego 2011:** 11 species, 21 reactions
  San Diego Mechanism, version 2011-11-22. http://combustion.ucsd.edu

Comparison of experimental data and simulation results

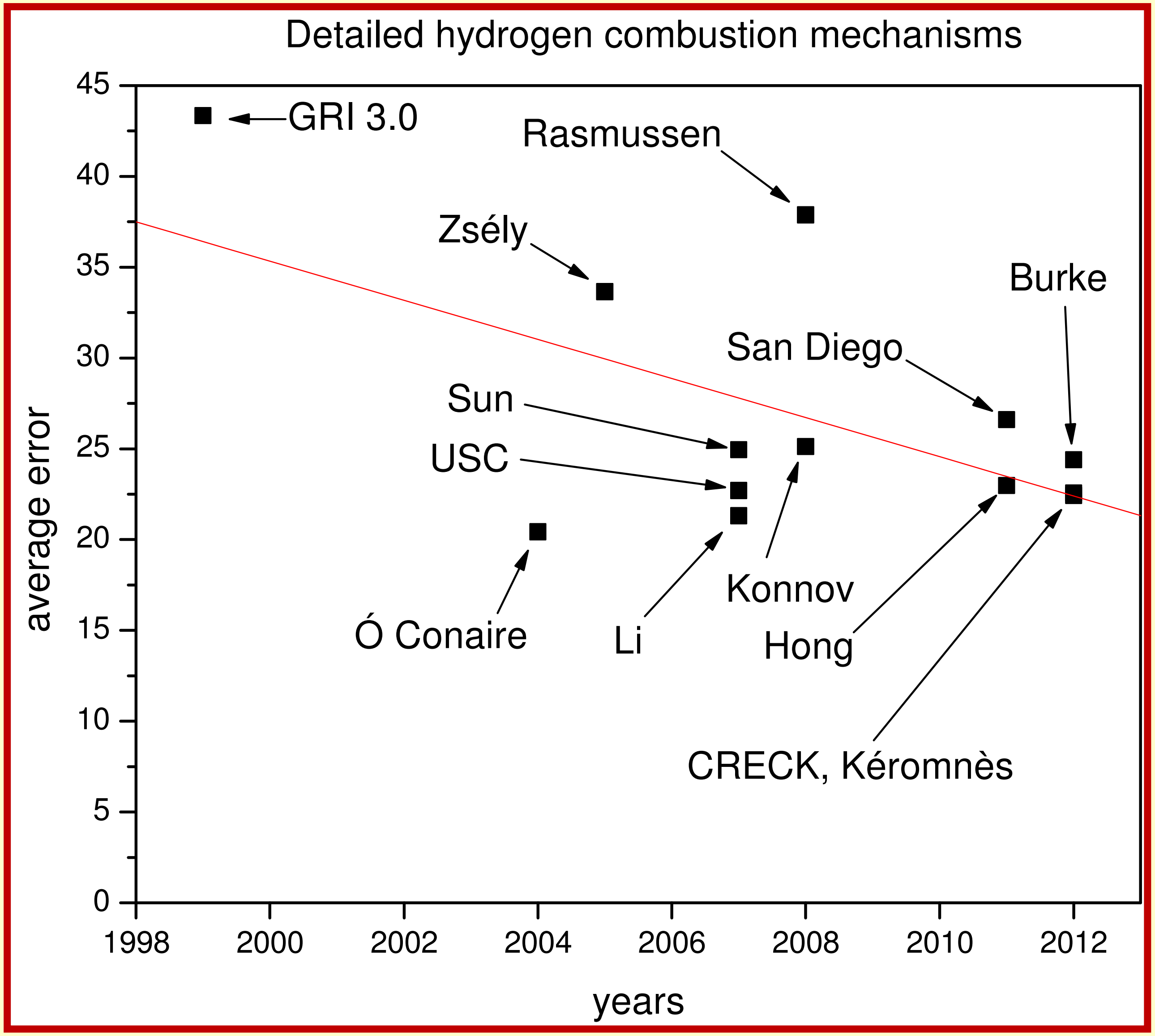
Objective function *Q* :

$$\boxed{Q(\mathbf{p}) = \frac{1}{N}\sum_{\mathrm{i}=1}^{N}\frac{1}{N_{\mathrm{i}}}\sum_{\mathrm{j}=1}^{N_{\mathrm{i}}}\left(\frac{Y_{\mathrm{ij}}^{\mathrm{mod}}(\mathbf{p}) - Y_{\mathrm{ij}}^{\mathrm{exp}}}{\sigma(Y_{\mathrm{ij}}^{\mathrm{exp}})}\right)^2}$$

$$Y_{ij} = \begin{cases} y_{ij} & \mathit{if}\ \sigma(y_{ij}^{\mathrm{exp}}) \approx \mathit{constant} \\ \ln y_{ij} & \mathit{if}\ \sigma(\ln y_{ij}^{\mathrm{exp}}) \approx \mathit{constant} \end{cases}$$

y_{ij}	measured/calculated rate coefficient OR measured/calculated ignition time/flame velocity in data point *j* of data series *i*
σ	standard deviation of the measured data
N_i	number of data points in data series *i*
N	number of data series (different experiments)

Performance of the mechanisms *vs.* years



Results of cross testing

average of error function values				Mechanism	Asaba *et al.* (1965) only
Ignition delays	PSR	flame	Overall performance		
48.13	26.34	32.67	43.34	GRI 3.0 1999	184.31
13.89	49.40	30.80	20.42	Ó Conaire 2004	122.88
21.87	83.19	54.34	33.64	Zsély 2005	143.30
14.00	54.57	32.32	21.31	Li 2007	154.69
17.87	65.83	29.27	24.94	Sun 2007	159.96
16.33	51.98	32.06	22.70	USC 2007 Version II	161.65
15.12	82.59	31.52	25.12	Konnov 2008	153.68
31.55	82.11	36.14	37.87	Rasmussen 2008	152.07
16.80	54.48	29.78	22.97	Hong 2011	165.11
20.77	55.60	33.65	26.61	San Diego 2011	181.05
18.69	52.15	31.66	24.39	Burke 2012	171.97
11.88	57.08	48.03	22.43	CRECK 2012	157.02
14.39	65.39	30.74	22.56	Kéromnès 2012	163.74
634	136	200	970	No. data points	37
53	8	19	80	No. datasets	3

Some indirect experimental data series are presumably wrong and these were excluded from the optimization and mechanism testing.

example: T. Asaba, W.C. Gardiner, R.F. Stubbelman,
Proc. Combust. Inst., **10**, 295-302(1965)

Step 3: Optimization of the rate parameters

1. **Direct and indirect measurements** are taken into account **simultaneously**.

2. The **uncertainty domain of all the Arrhenius parameters** is determined

3. For each important reaction step, the Arrhenius parameters ***A*, *n*, *E*** and maybe other rate parameters are determined within their domain of uncertainty.

Turányi T, Nagy T, Zsély IGy, Cserháti M, Varga T, Szabó B,
Sedyó I, Kiss P, Zempléni A, Curran H J
Determination of rate parameters based on both direct and indirect measurements.
Int. J. Chem. Kinet. **44**, 284–302 (2012)

Optimization and uncertainty estimation of parameters

Optimization = minimization of this error function:

$$\boxed{E(\mathbf{p}) = \sum_{\mathrm{i}=1}^{N} \frac{w_{\mathrm{i}}}{N_{\mathrm{i}}} \sum_{\mathrm{j}=1}^{N_{\mathrm{i}}} \left(\frac{\ln y_{\mathrm{ij}}^{\mathrm{mod}}(\mathbf{p}) - \ln y_{\mathrm{ij}}^{\mathrm{exp}}}{\sigma(\ln y_{\mathrm{ij}}^{\mathrm{exp}})} \right)^2}$$

y_k measured/calculated rate coefficient **OR**
measured/simulated indirect measurement

Calculation of the covariance matrix of the estimated parameters:

$$\boxed{\mathbf{\Sigma_p} = \left[\left(\mathbf{J}_{\mathrm{o}}^{\mathrm{T}} \mathbf{W} \mathbf{\Sigma}_{\mathbf{Y}}^{-1} \mathbf{J}_{\mathrm{o}} \right)^{-1} \mathbf{J}_{\mathrm{o}}^{\mathrm{T}} \mathbf{W} \mathbf{\Sigma}_{\mathbf{Y}}^{-1} \right] \left(\mathbf{\Sigma}_{\mathbf{Y}} + \mathbf{\Sigma}_{\Delta} \right) \left[\left(\mathbf{J}_{\mathrm{o}}^{\mathrm{T}} \mathbf{W} \mathbf{\Sigma}_{\mathbf{Y}}^{-1} \mathbf{J}_{\mathrm{o}} \right)^{-1} \mathbf{J}_{\mathrm{o}}^{\mathrm{T}} \mathbf{W} \mathbf{\Sigma}_{\mathbf{Y}}^{-1} \right]^{\mathrm{T}}}$$

Transformation of the covariance matrix of parameters to „traditional” gas kinetics measures of uncertainty

covariance matrix of Arrhenius parameters → covariance matrix of ln *k*

$$\boxed{\operatorname{cov}\left(\kappa_i(T),\kappa_j(T)\right)=\overline{(\kappa_i(T)-\overline{\kappa}_i(T))(\kappa_j(T)-\overline{\kappa}_j(T))}=\Theta^T\,\overline{(p_i-\overline{p}_i)(p_j-\overline{p}_j)^T}\,\Theta=\Theta^T\Sigma_{p_i,p_j}\Theta}$$

$$\boxed{\theta^T := \left[1 \quad \ln\theta \quad -\theta^{-1}\right]}$$

$$\boxed{\sigma(\ln k)=\ln 10\,\sigma(\log_{10} k)=\frac{\ln 10}{m_f}f(T)}$$

covariance matrix of ln *k* → correlation *r* between the ln *k* values

$$\boxed{r_{\kappa_i,\kappa_j}(T)=\frac{\operatorname{cov}\left(\kappa_i(T),\kappa_j(T)\right)}{\sigma_{\kappa_i}(T)\,\sigma_{\kappa_j}(T)}}$$

Strategy for optimization

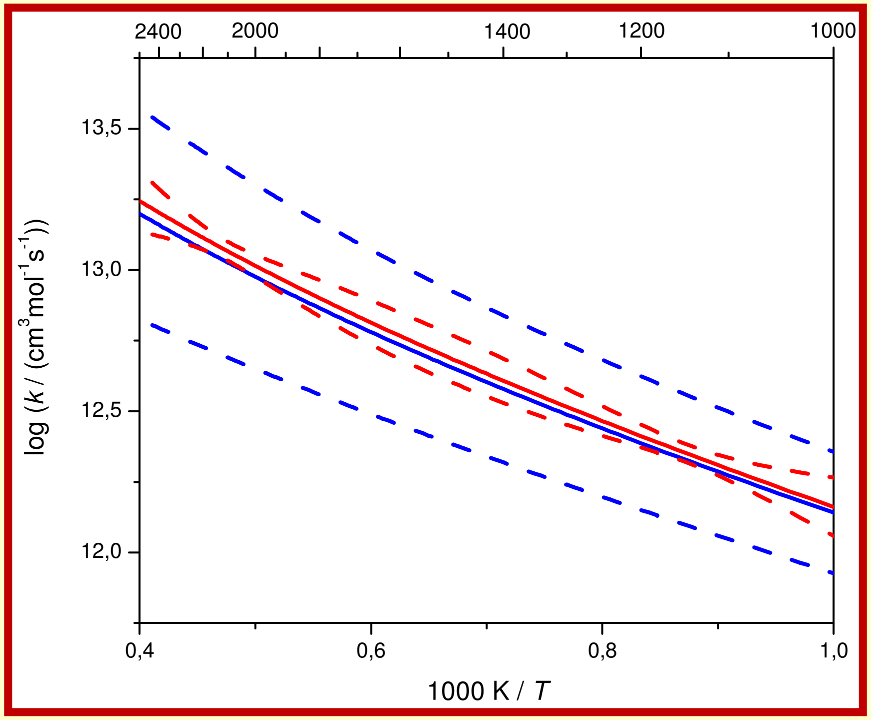
	experiment	number of datapoints	H+O2=O+OH	LPH+O2(+M)=HO2(+M)	O+H2=H+OH	OH+H2=H+H2O	H2O2+H=H2+HO2	HO2+H=2OH	HO2+H=H2+O2	HO2+OH<=>H2O+O2
STEP1	Herzler et al. (2009^{a})	9	O	O						
	Fujimoto and Suzuki (1967)	9	O	O						
	Zhang et. al. (2012^{a})	7	O	O						
	Naumann et. al. (2011^{a})	19	O	O						
	Naumann et. al. (2011^{b})	26	O	O						
STEP2	Petersen et al. (2003^{a})	9	O		O					
	Cheng and Oppenheim (1984^{a})	58	O		O					
	Petersen et al. (2003^{b})	24	O		O					
	Petersen et al. (2003^{c})	4	O		O					
	Petersen et al. (1996^{a})	16	O	O	O					
	Petersen et al. (1996^{b})	6	O	O	O					
	Slack (1977)	12	O	O	O					
	Bhaskaran et al. (1973)	14	O	O	O					
	Wang et al. (2003^{a})	12	O	O	O					
	Naumann et. al. (2011^{c})	13	O	O	O					
STEP3	Chaumeix et al. (2007^{a})	5	O		O	O				
	Chaumeix et al. (2007^{b})	7	O		O	O				
	Chaumeix et al. (2007^{c})	5	O		O	O				
	Cohen et. al. (1967)	21	O		O	O				
	Cheng and Oppenheim (1984^{b})	56	O	O	O	O				
	Naumann et. al. (2011^{d})	19	O	O	O	O				
	Naumann et. al. (2011^{e})	19	O	O	O	O				

STEP 2	Petersen et al. (2003^{a})	9	O		O					
	Cheng and Oppenheim (1984^{a})	58	O		O					
	Petersen et al. (2003^{b})	24	O		O					
	Petersen et al. (2003^{c})	4	O		O					
	Petersen et al. (1996^{a})	16	O	O	O					
	Petersen et al. (1996^{b})	6	O	O	O					
	Slack (1977)	12	O	O	O					
	Bhaskaran et al. (1973)	14	O	O	O					
	Wang et al. (2003^{a})	12	O	O	O					
	Naumann et. al. (2011^{c})	13	O	O	O					
STEP 3	Chaumeix et al. (2007^{a})	5	O		O	O				
	Chaumeix et al. (2007^{b})	7	O		O	O				
	Chaumeix et al. (2007^{c})	5	O		O	O				
	Cohen et. al. (1967)	21	O		O	O				
	Cheng and Oppenheim (1984^{b})	56	O	O	O	O				
	Naumann et. al. (2011^{d})	19	O	O	O	O				
	Naumann et. al. (2011^{e})	19	O	O	O	O				
STEP 4	Zhang et. al. (2012^{b})	10	O	O			O			
	Wang et al. (2003^{b})	10	O	O			O			
	Wang et al. (2003^{c})	21	O	O			O			
	Naumann et. al. (2011^{f})	9	O	O	O		O			
STEP 5	Wang et al. (2003^{d})	12	O	O			O	O		
	Naumann et. al. (2011^{g})	10	O	O			O	O		
	Petersen et al. (1996^{c})	8	O	O			O	O		
	Herzler et al. (2009^{b})	9	O	O			O	O		
	Petersen et al. (1996^{d})	3	O	O		O	O	O		
	Zhang et. al. (2012^{c})	8	O	O			O	O		
	Herzler et al. (2009^{c})	12	O	O			O	O		
	Naumann et. al. (2011^{h})	16	O	O			O	O		
STEP 6	Petersen et al. (1996^{e})	14	O		O				O	
	Petersen et al. (1996^{f})	7	O	O	O				O	
	Schott and Kinsey (1958)	17	O		O	O			O	
	Petersen et al. (1996^{g})	17	O	O	O				O	
	Naumann et. al. (2011^{i})	18	O	O	O	O			O	
	Naumann et. al. (2011^{j})	13	O	O	O	O	O	O		O

Results of optimization

- A new set of optimized rate parameters
  (in this case: 26 optimized parameters (23 Arrhenius parameters of 8 reactions
  3 third body efficiencies)

- Covariance matrix of all optimized parameters
  CONVERTED TO
- *f*(*T*) uncertainty function for each rate coefficient
- *r*(*T*) correlation function of pairs of rate coefficients



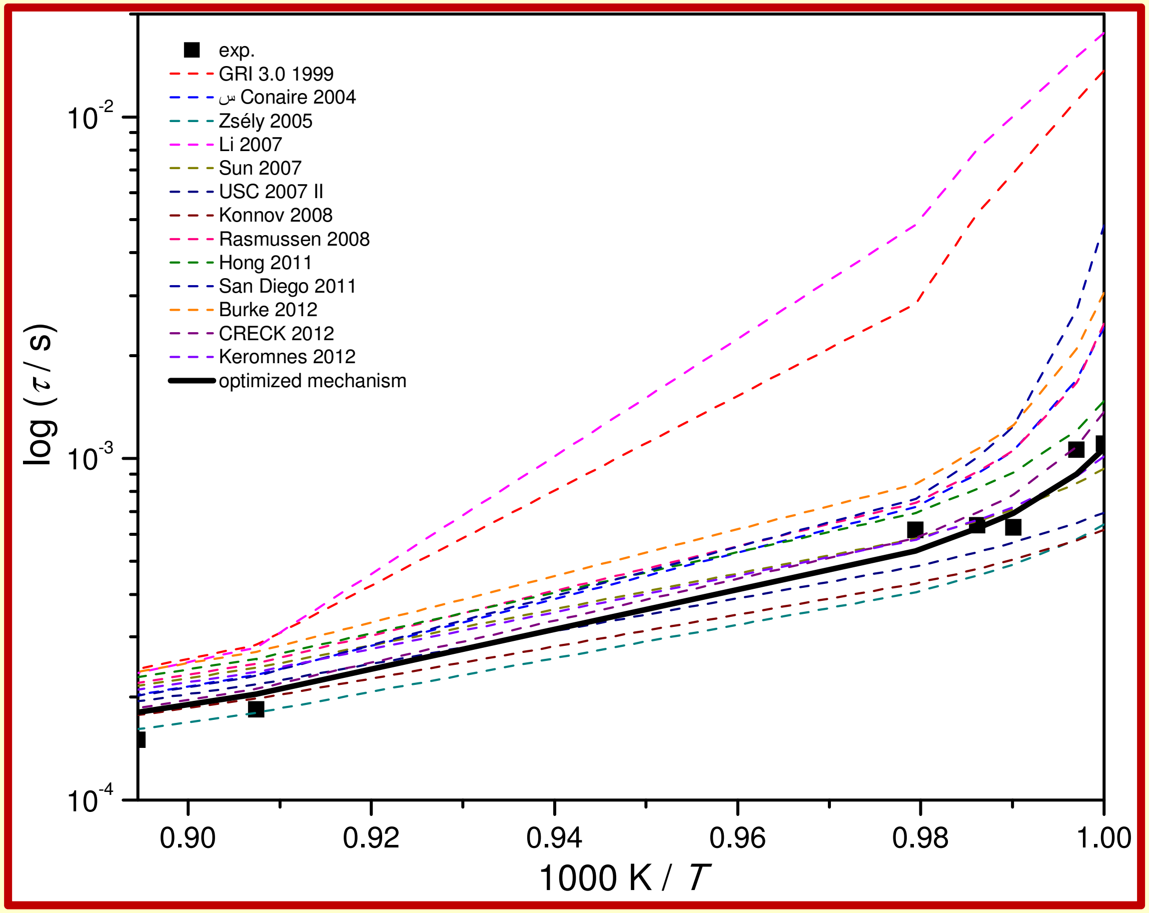
reaction $OH+H_2=H_2O+H$:

—— literature *k* value
- - - - literature *k* uncertainty

—— optimized *k* value
- - - - optimized *k* uncertainty

Step 4: Testing the optimized mechanism against other mechanisms

The optimization code created figures on
the agreement of the simulation results and the experimental points.



experiments: Pang, G.A., Davison, D.F., Hanson, R.K.,
Proc. Combust. Inst., **32**, 181-188(2009)
Fig. 3., full square; 4% H2 / 2% O2 / Ar, $P_{t=0}$ = 3.5 atm

Testing the optimized mechanism against other mechanisms

mechanisms	**set #1**		
GRI 3.0 1999	43.63		
Ó Conaire 2004	11.01		
Zsély 2005	16.64		
Li 2007	11.47		
Sun 2007	15.72		
USC 2007 II	14.31		
Konnov 2008	12.42		
Rasmussen 2008	28.58		
Hong 2011	14.44		
San Diego 2011	18.18		
Burke 2012	16.49		
CRECK 2012	9.28		
Kéromnès 2012	11.94		
optimized mechanism	**8.25**		

error function values (smaller is better)

set #1: Ignition time experiments *used at the optimization*

Testing the optimized mechanism against other mechanisms

mechanisms	**set #1**	**set#2**	
GRI 3.0 1999	43.63	48.13	
Ó Conaire 2004	11.01	13.89	
Zsély 2005	16.64	21.87	
Li 2007	11.47	14.00	
Sun 2007	15.72	17.87	
USC 2007 II	14.31	16.33	
Konnov 2008	12.42	15.12	
Rasmussen 2008	28.58	31.55	
Hong 2011	14.44	16.80	
San Diego 2011	18.18	20.77	
Burke 2012	16.49	18.69	
CRECK 2012	9.28	11.88	
Kéromnès 2012	11.94	14.39	
optimized mechanism	**8.25**	**11.59**	

set #1: Ignition time experiments *used at the optimization*

set #2: All available ignition time experiments

Testing the optimized mechanism against other mechanisms

mechanisms	**set #1**	**set#2**	**set#3**
GRI 3.0 1999	43.63	48.13	43.34
Ó Conaire 2004	11.01	13.89	20.42
Zsély 2005	16.64	21.87	33.64
Li 2007	11.47	14.00	21.31
Sun 2007	15.72	17.87	24.94
USC 2007 II	14.31	16.33	22.70
Konnov 2008	12.42	15.12	25.12
Rasmussen 2008	28.58	31.55	37.87
Hong 2011	14.44	16.80	22.97
San Diego 2011	18.18	20.77	26.61
Burke 2012	16.49	18.69	24.39
CRECK 2012	9.28	11.88	22.43
Kéromnès 2012	11.94	14.39	22.56
optimized mechanism	**8.25**	**11.59**	**19.35**

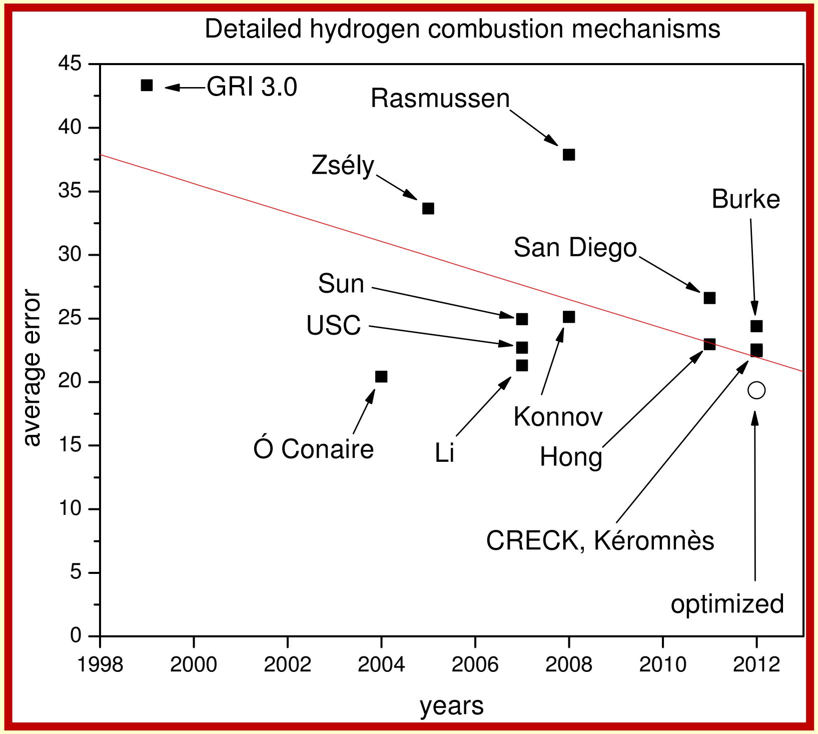
set #1: Ignition time experiments *used at the optimization*

set #2: All available ignition time experiments

set #3: All types of data (ignition time, PSR, laminar flame velocity)

Testing the optimized mechanism against other mechanisms

mechanisms	**set #1**	**set#2**	**set#3**
GRI 3.0 1999	43.63	48.13	43.34
Ó Conaire 2004	11.01	13.89	20.42
Zsély 2005	16.64	21.87	33.64
Li 2007	11.47	14.00	21.31
Sun 2007	15.72	17.87	24.94
USC 2007 II	14.31	16.33	22.70
Konnov 2008	12.42	15.12	25.12
Rasmussen 2008	28.58	31.55	37.87
Hong 2011	14.44	16.80	22.97
San Diego 2011	18.18	20.77	26.61
Burke 2012	16.49	18.69	24.39
CRECK 2012	9.28	11.88	22.43
Kéromnès 2012	11.94	14.39	22.56
optimized mechanism	**8.25**	**11.59**	**19.35**

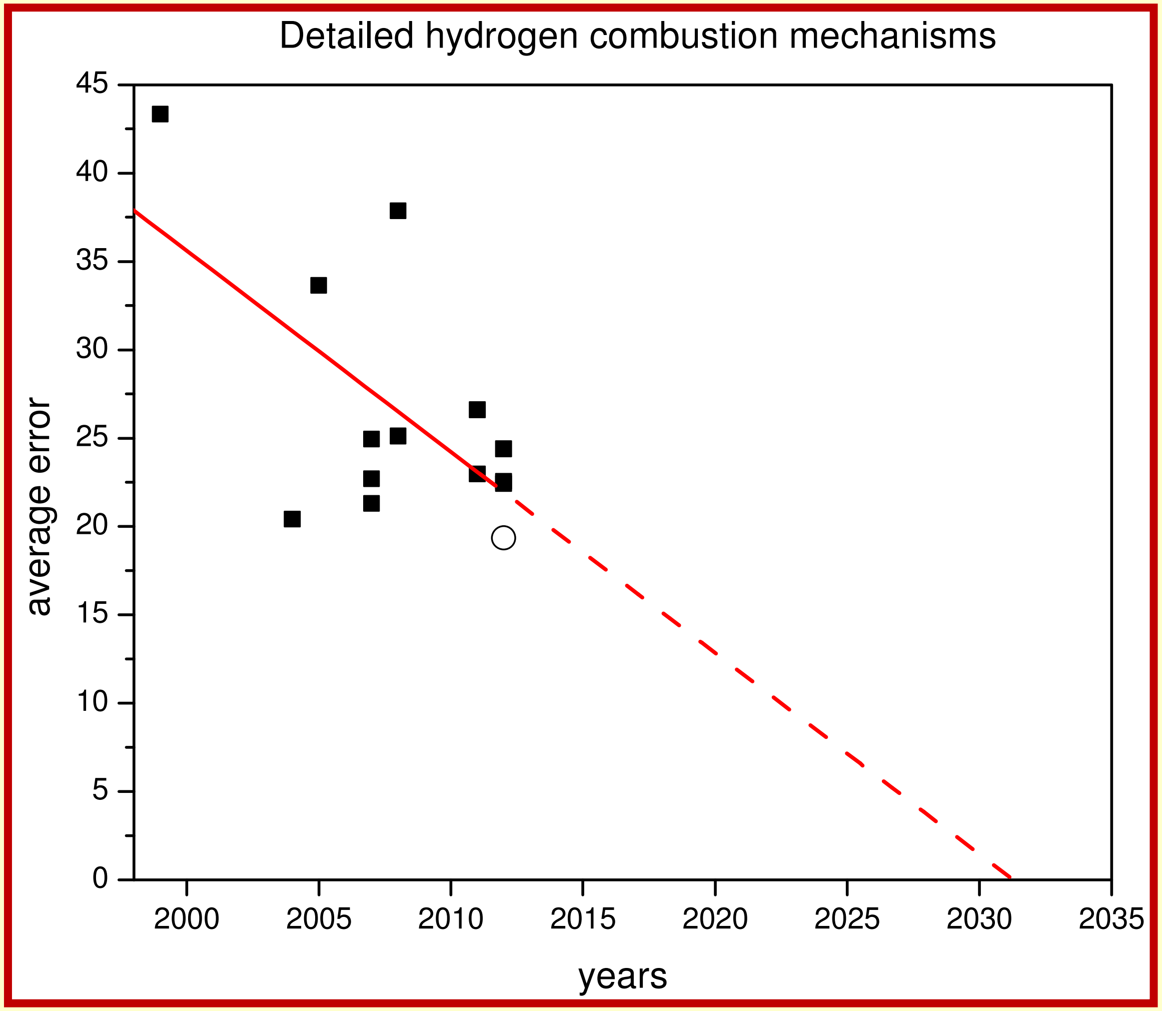


set #1: Ignition time experiments *used at the optimization*

set #2: All available ignition time experiments

set #3: All types of data (ignition time, PSR, laminar flame velocity)

The future



Based on the current trend,

the absolutely accurate hydrogen combustion mechanism

will be available on **7th March, 2032** ☺

Summary

1 The *f*(*T*) uncertainty parameters available from the data collections are realistic, but have several shortcomings, like it refers to the uncertainty of *k* only.
Needed: a joint uncertainty of the rate parameters.

2 Assessment of the **joint uncertainty domain of the Arrhenius parameters** of a selected reaction step based on **all direct measurements and TST calculations.**
- upper estimation of the uncertainty
- no information about the correlation of two *k* values

3 Comprehensive evaluation of the uncertainty of all rate parameters:
For a given chemical kinetic system,
all direct, indirect and theoretical results are collected
assessment of the uncertainty of input data
⇒ **new, physically meaningful rate parameters**
⇒ **information about the joint uncertainty of rate parameters**

⇒ **better simulation results**
⇒ **quantification of the uncertainty of the simulation results**

Acknowledgement

For the helpful discussions

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COST CM0901 Detailed Chemical Models for Cleaner Combustion

OTKA T68256, OTKA K84054

Thank you all

for your attention!

Energy and Resources Research Institute

Faculty of Engineering

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The role of uncertainty quantification within kinetic model improvement in combustion

Alison S. Tomlin

Development of complex kinetic mechanisms

In combustion complex chemical mechanisms built by:

- ➢ proposing sets of rules for species interactions:

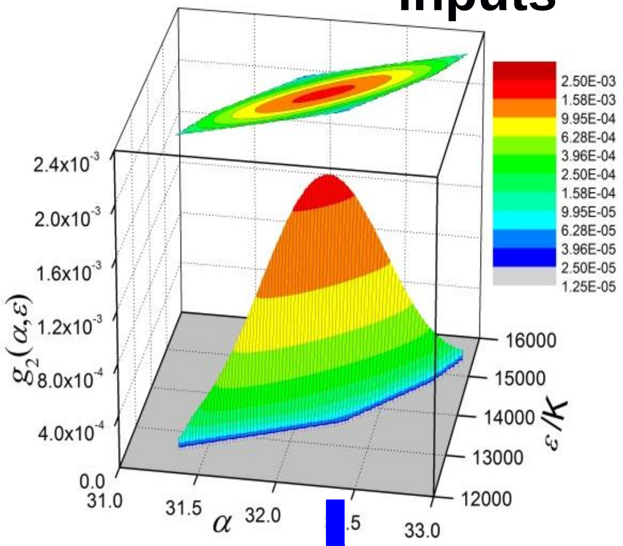
  mechanism protocol.

- ➢ developing **effective parameterisations** for the kinetics described within the mechanism.

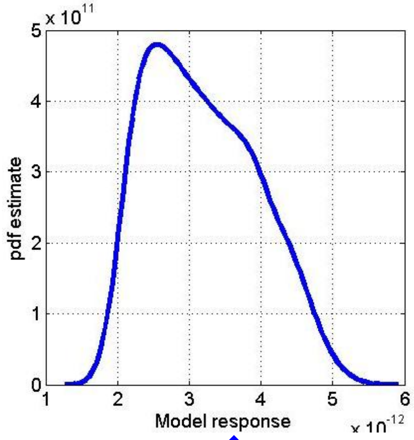
- Ability to specify protocols well developed e.g. hydrocarbon oxidation.
- Large comprehensive mechanisms e.g. biodiesel surrogate methyl decanoate: 3012 sp., 8820 reacs (Herbinet et al., 2008)
- Many rate coefficients have to initially be estimated using rules related to chemical structure.
- **Does this lead to a robust mechanism? How can the model robustness be improved?**

Improving model robustness

Joint pdf of inputs



Probability distribution of predicted Y_i



We would like to narrow the output distribution as far as possible i.e. to reduce predictive error bars.

Sensitivity and uncertainty analysis

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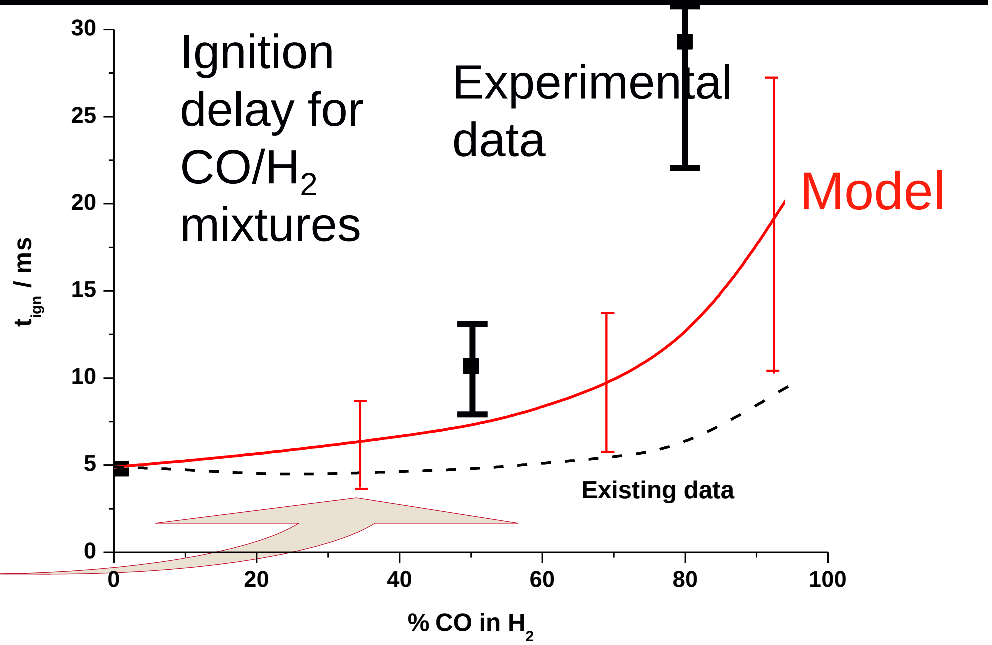
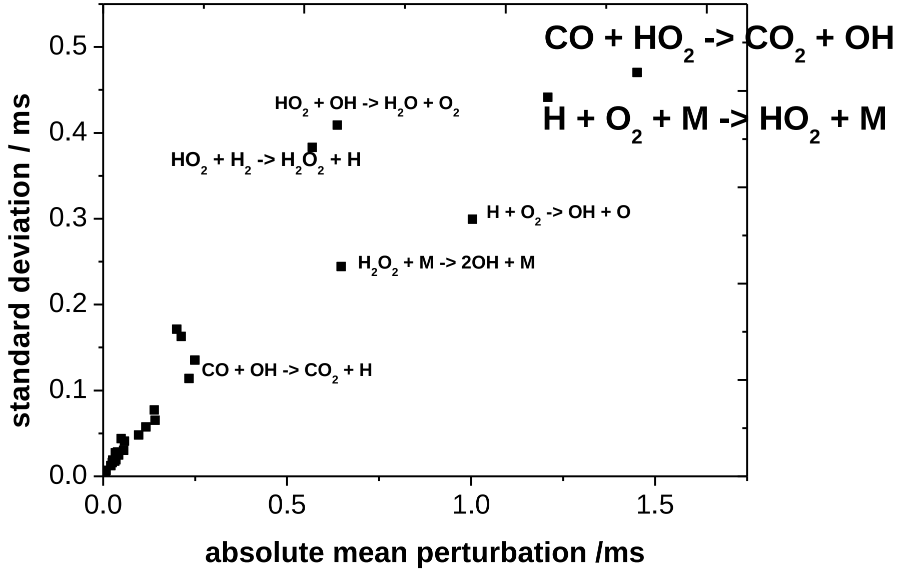
- **Uncertainty analysis (UA)** puts error bars on predictions.
- Overlap (or not) with experimental values tells us whether our model may be structurally robust.

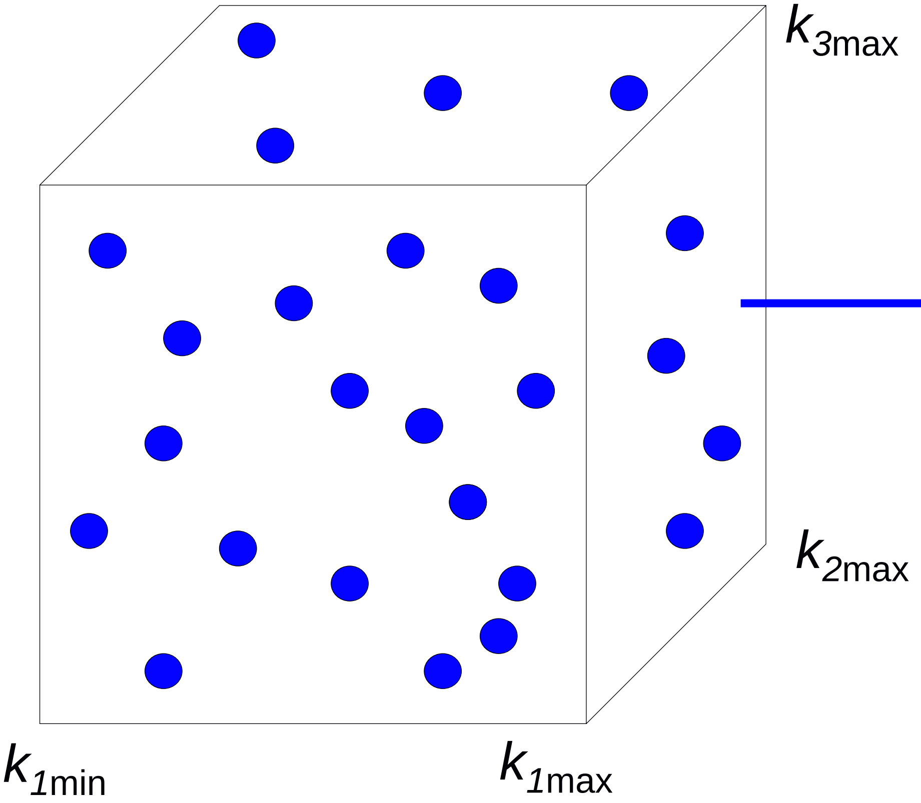


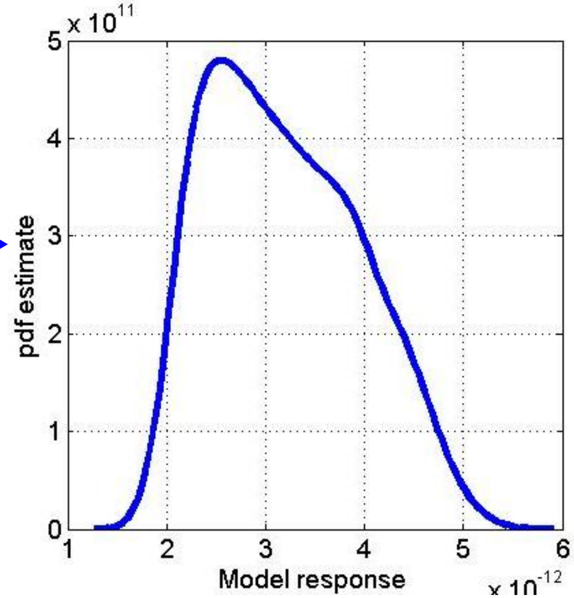


Sensitivity analysis (SA) tries to determine how much each input parameter contributes to the output uncertainty (usually variance).

Global sensitivity/uncertainty methods

Global - attempts to cover whole input space using a sampling method.


$k_{3\max}$
$k_{2\max}$
$k_{1\min}$
$k_{1\max}$



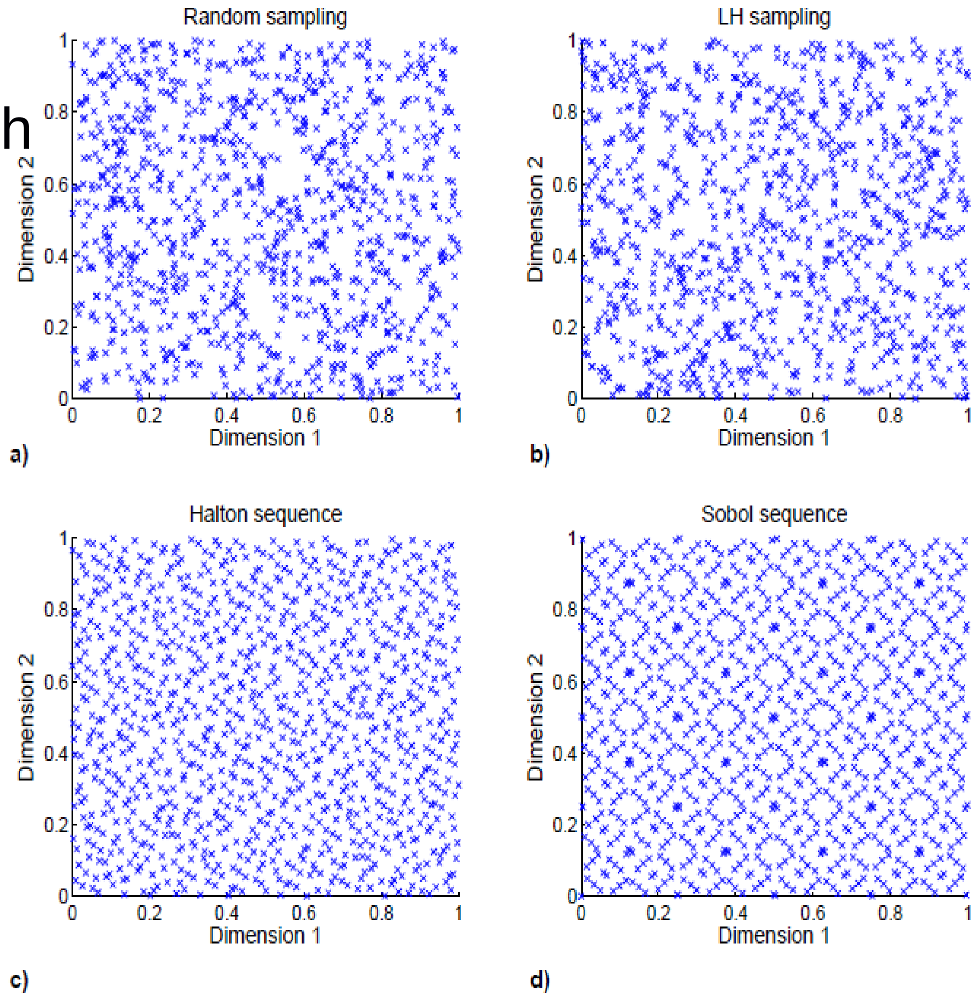
Why global methods?

Sampling methods can be computationally costly so why bother.

- To simulate output distributions for available targets.
- To calculate the contribution of important parameters to these distributions however large their uncertainty ranges.
- To see how each target helps to constrain a parameter
  - ➢ Could be important for the use of optimisation approaches where parameter isolation helps to narrow constraints.
- To explore parameter interactions.

Sampling approaches

- Need efficient sampling approach where the output moments converge quickly with sample size.
- Quasi-random approaches usually work best.
- Sample from input distributions until predicted output mean and variance converge.
- Then need a method to investigate input-output relationships.



High Dimensional Model Representations (HDMR)

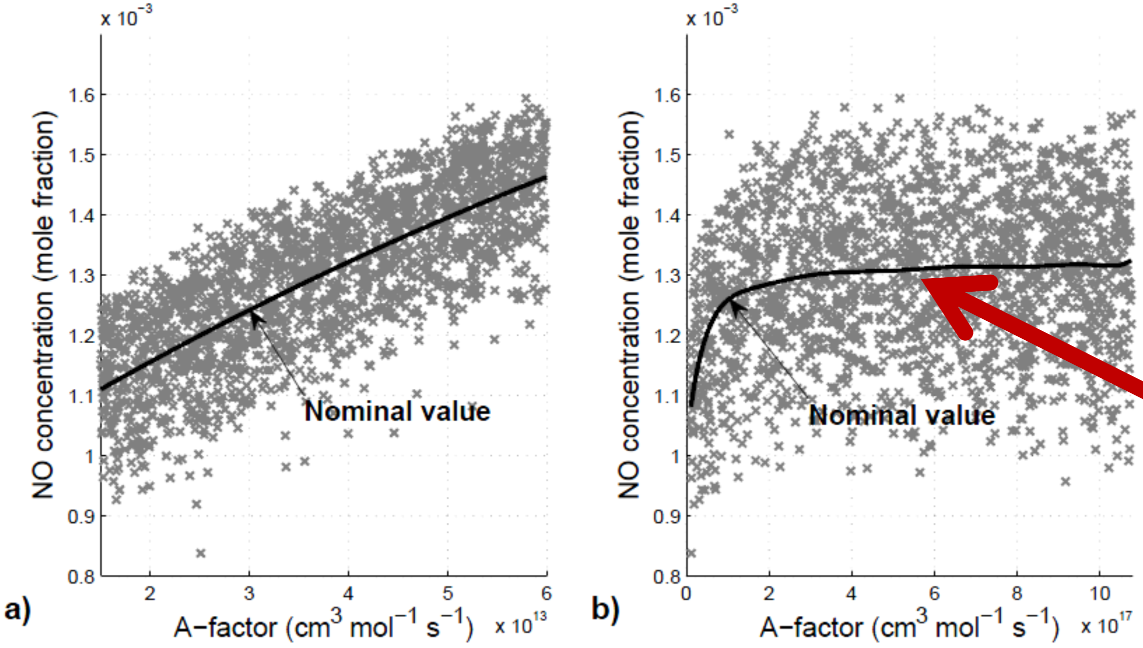
- Input-output relationship is expressed as a finite hierarchical function expansion:

$$f(\mathbf{x}) \equiv f_0 + \sum_{i=1}^{n} f_i(x_i) + \sum_{1 \le i \le j \le n} f_{ij}(x_i, x_j) + \ldots + \mathrm{f}_{12\ldots\mathrm{n}}(x_1, x_2, \ldots, x_n)$$

- Model replacement built using quasi random sample and approximation of component functions by orthonormal polynomials.
- Equivalent to ANOVA distribution so each term represents contribution to overall output variance.
- 1st & 2nd order sensitivity indices easily calculated from polynomial coefficients.

Monte Carlo (MC) simulations

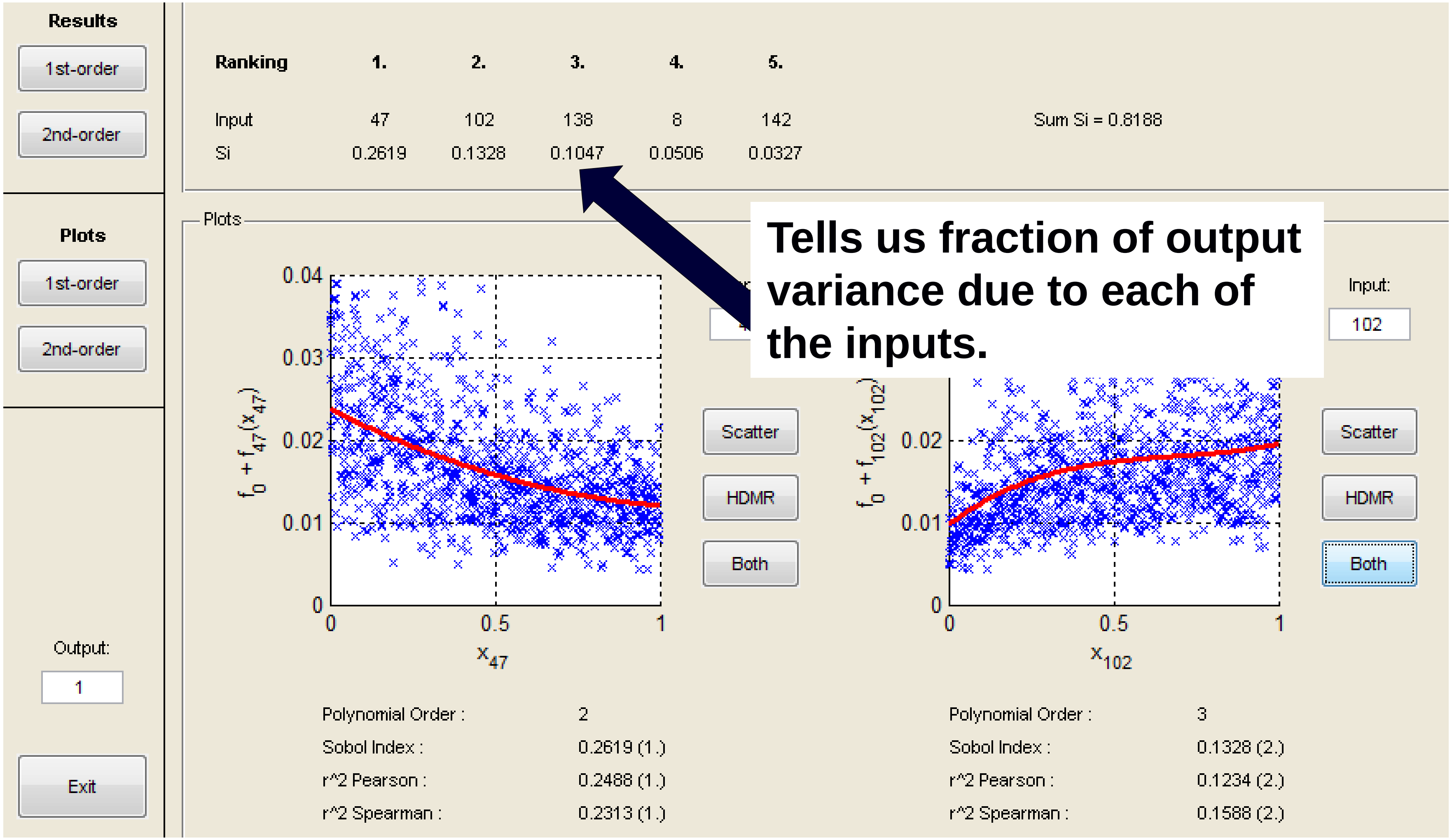
- Component functions reveal independent mean effect of each parameter and highlight any non-linear responses.
- Local S'_i at the nominal value may be quite different from the overall effect across the feasible parameter range.
- Scatter reveals influence of other parameters.



Example from flame calculation: NOx prediction.

Highly nonlinear

1st order sensitivities and ranking + component functions



Ranking	1.	2.	3.	4.	5.
Input	47	102	138	8	142
Si	0.2619	0.1328	0.1047	0.0506	0.0327

Sum Si = 0.8188

Output: 1

Input: 102

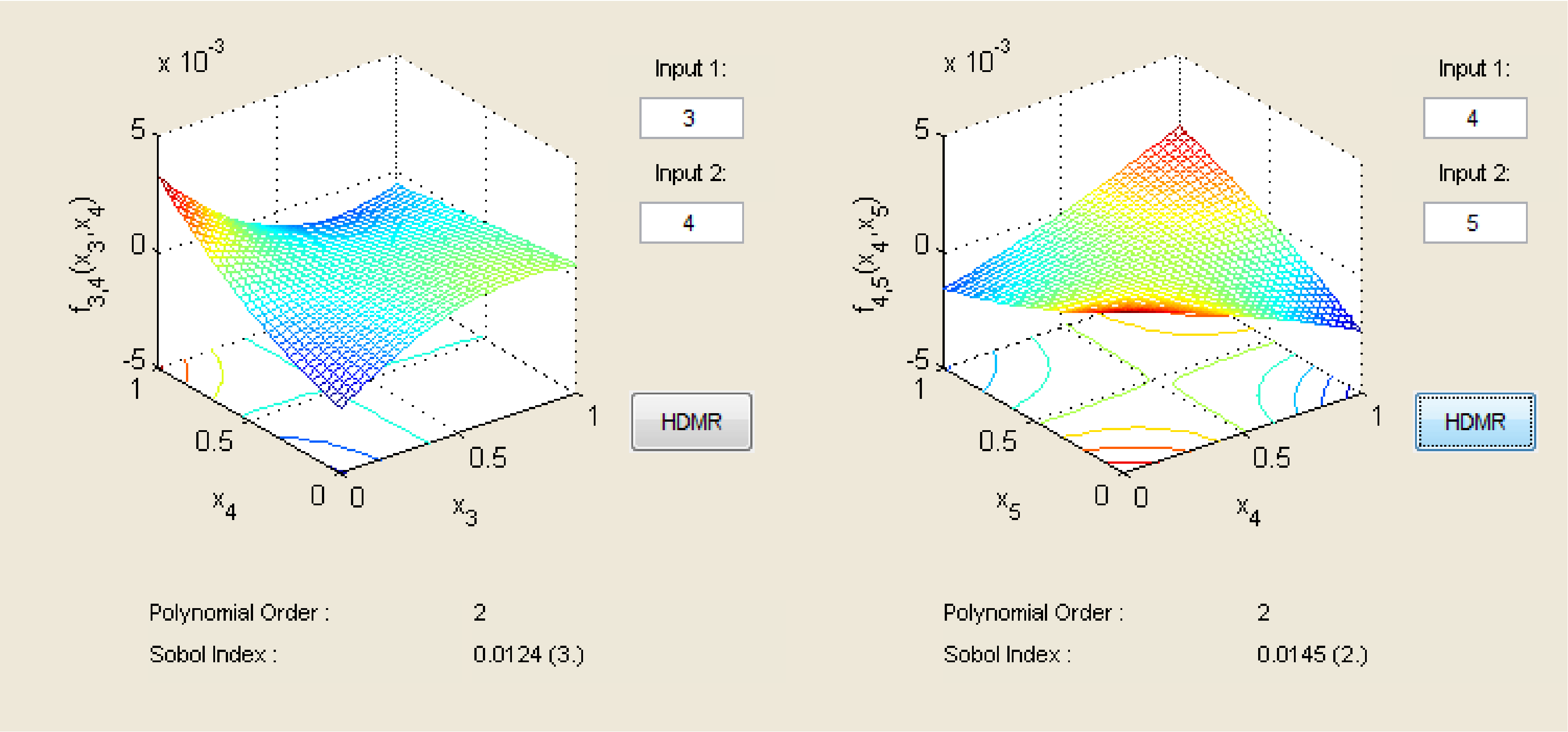
Polynomial Order :	2
Sobol Index :	0.2619 (1.)
r^2 Pearson :	0.2488 (1.)
r^2 Spearman :	0.2313 (1.)

Polynomial Order :	3
Sobol Index :	0.1328 (2.)
r^2 Pearson :	0.1234 (2.)
r^2 Spearman :	0.1588 (2.)

Results
1st-order
2nd-order
Plots
1st-order
2nd-order
Exit
0.04
0.03
0.02
0.01
0
0.5
1
$f_0 + f_{47}(x_{47})$
x_{47}
Scatter
HDMR
Both
$f_0 + f_{102}(x_{102})$
x_{102}
Scatter
HDMR
Both

Tells us fraction of output variance due to each of the inputs.

2nd order component functions


x 10-3
5
0
-5
$f_{3,4}(x_3,x_4)$
1
0.5
0
x_4
0
0.5
1
x_3
HDMR
x 10-3
5
0
-5
$f_{4,5}(x_4,x_5)$
1
0.5
0
x_5
0
0.5
1
x_4
HDMR

Input 1: 3
Input 2: 4

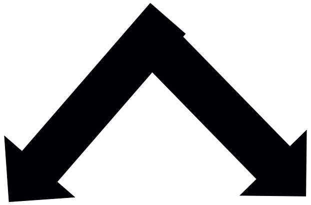
Polynomial Order : 2
Sobol Index : 0.0124 (3.)

Input 1: 4
Input 2: 5

Polynomial Order : 2
Sobol Index : 0.0145 (2.)

Typical practice

- Constructed mechanism incorporated within model which simulates chosen experimental targets:
  - ➢ flame speeds, ignition delays, JSR concentration profiles
- Agreement with targets assessed and sensitivity analysis performed.



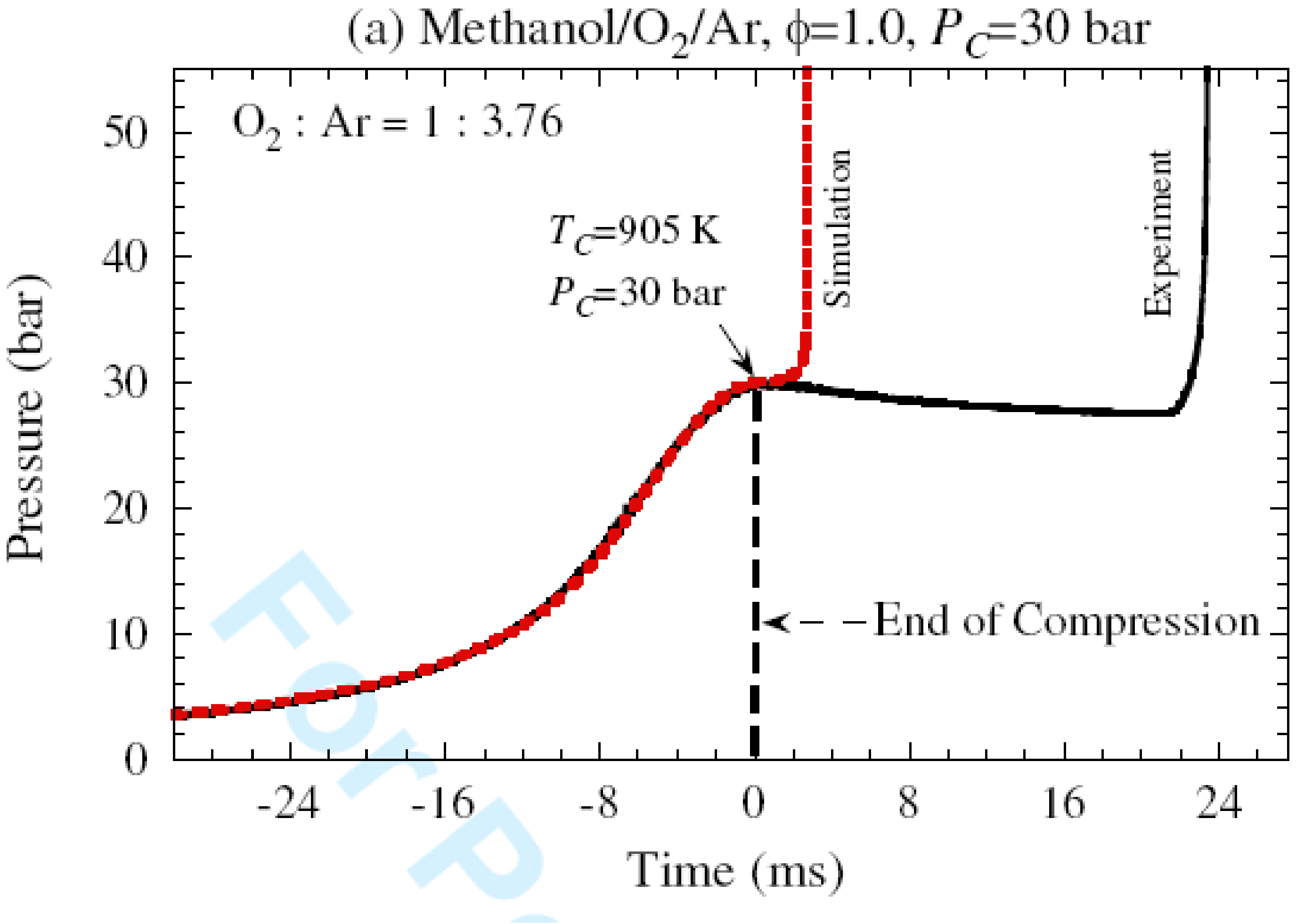
Updates made to key parameters e.g. through theory or direct experiments

Mechanism optimised using available targets from indirect experiments

Example 1

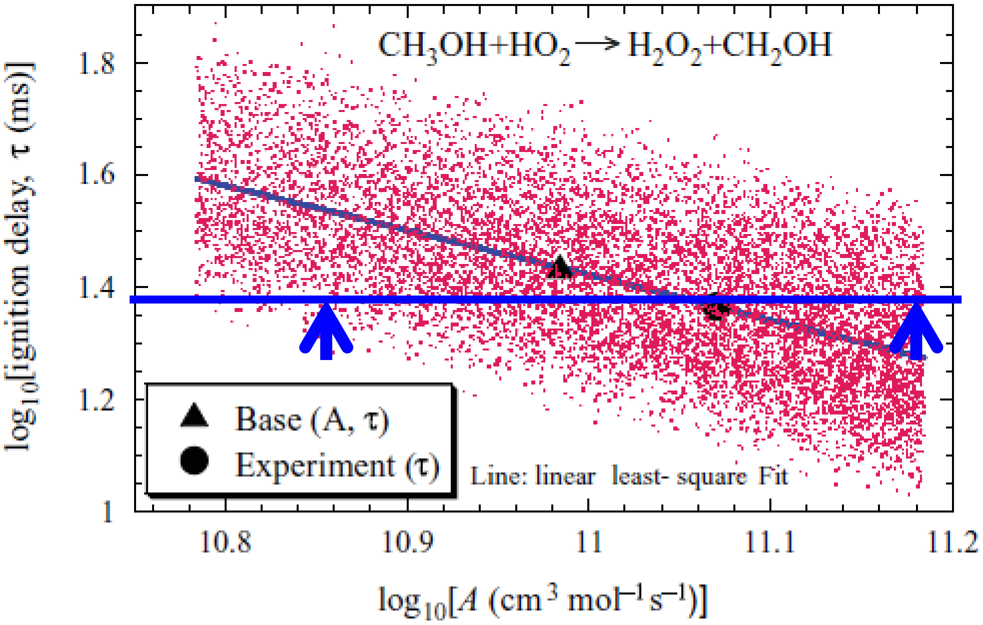
Methanol oxidation

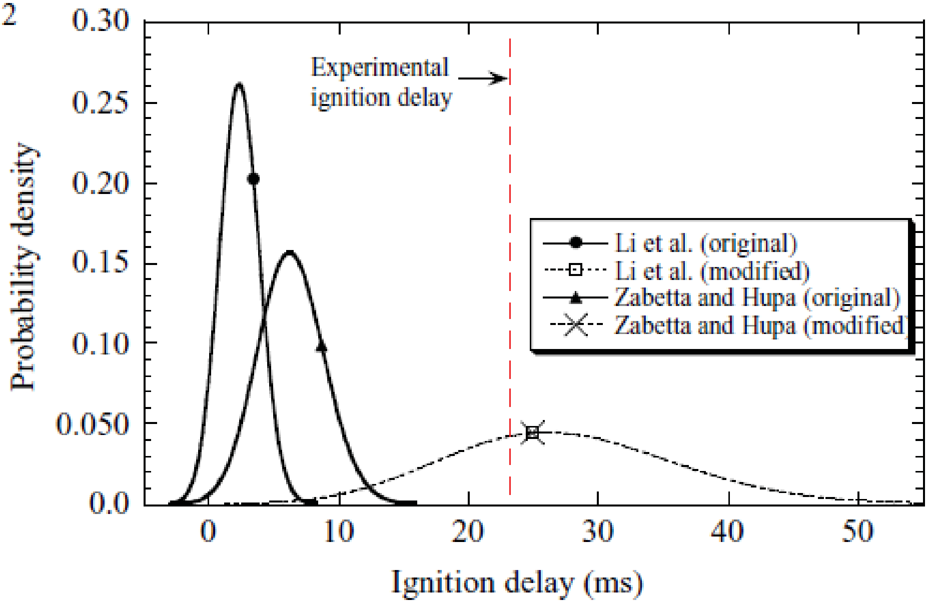
Comparison of simulated ign. delays (Li et al. 2007) with data (Kumar & Sung, 2011)



For P

Constraints from the experiments?





Impact of modifying rate to Tsang value

Theoretical study of Skodje et al. (2010)

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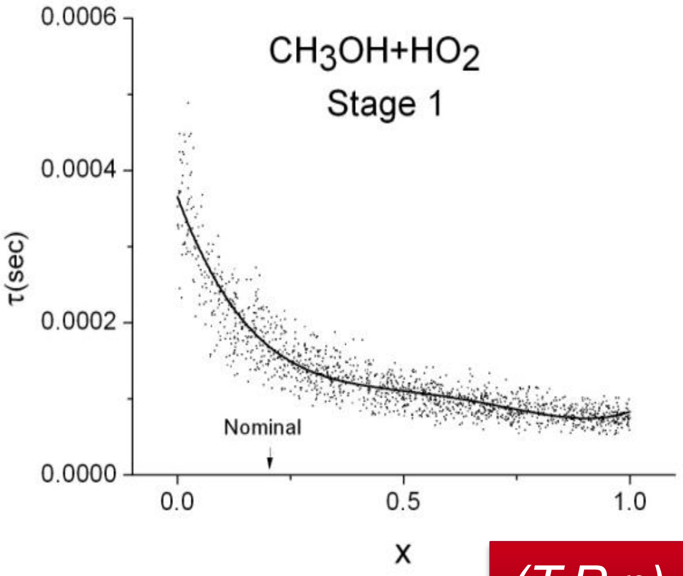
- Mechanism - Li et al. (2007); 18 species, 93 reactions.
- Target output - ignition delay time (τ) for stoichiometric mixtures of methanol and oxygen over a range of temperatures and pressures.
- Enthalpies of formation and *A*-factors varied over random sample.
- Using initial ranges one reaction dominates (up to 90% of total output variance) with strong **nonlinearities**.

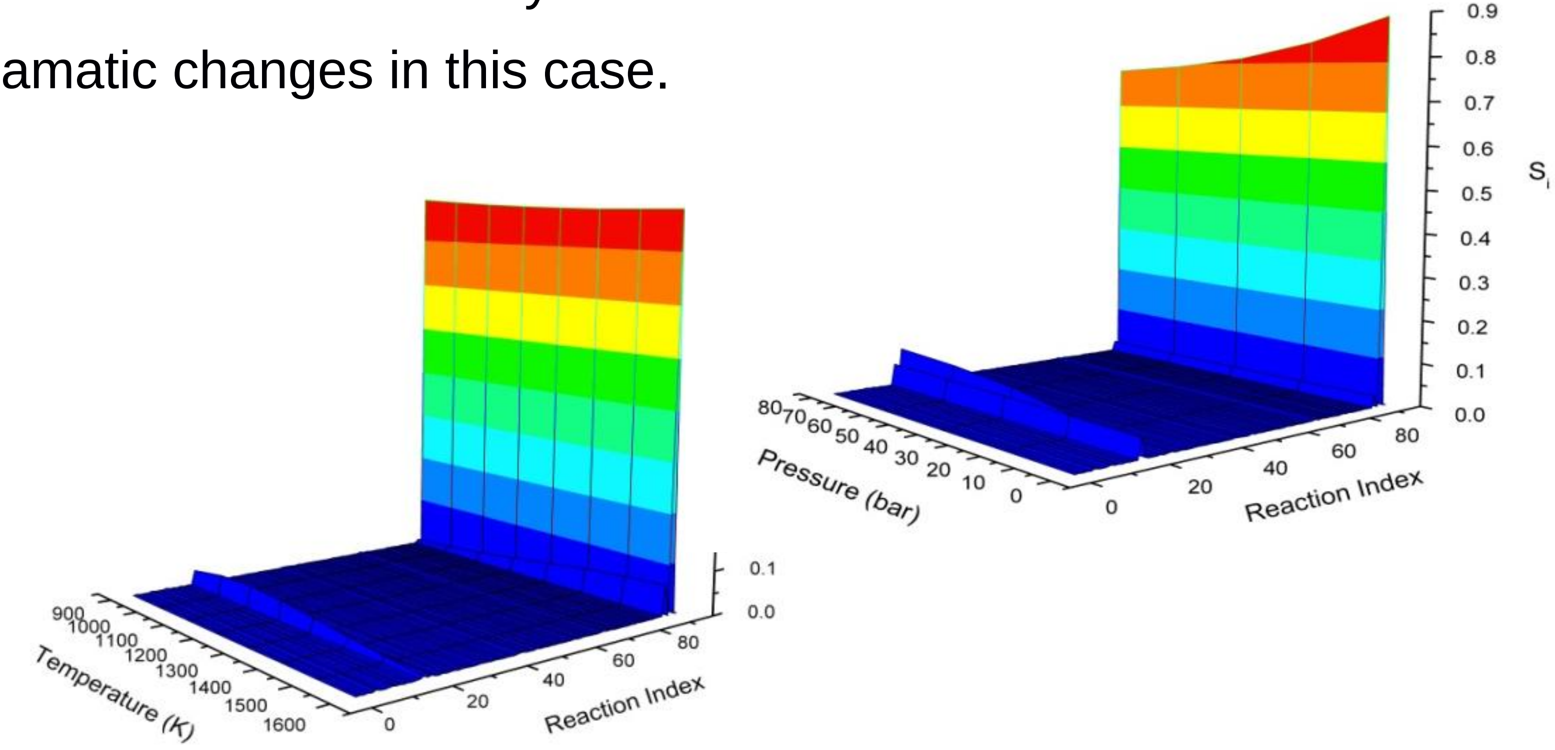
Low scatter indicates low influence of all other parameters.



(T,P,φ)=(1150K,5bar,1)

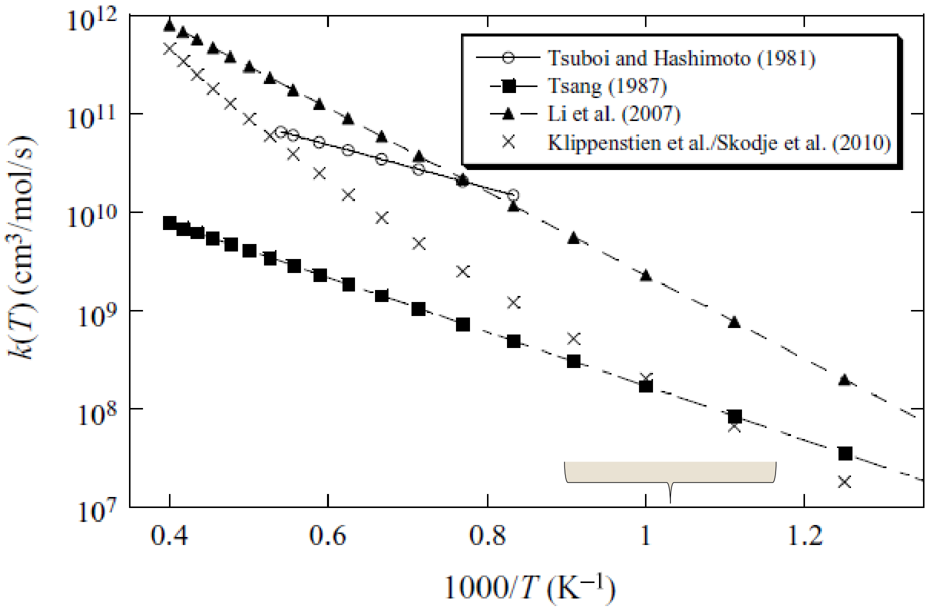
Sensitivity mapping over *P*/*T*

- Can also test how sensitivities change outside of conditions where experimental data exists - although uncertainties in activation energies were not included in this study.
- No dramatic changes in this case.



Model Updates

- CH_3OH+HO_2 a key reaction with initial uncertainty (10^f) of 5.
- Transition state theory (TST) and variational TST (VTST) then used to re-estimate its rate coefficient (Klippenstein,2011).
- Lower than value in Li at low *T* (**8 times i.e. larger than 5!**) with an **estimated** uncertainty of 2.



- Close agreement between new value and that of Tsang at low temperatures.
- Closer to Li value at high temperatures.

Results of model updates

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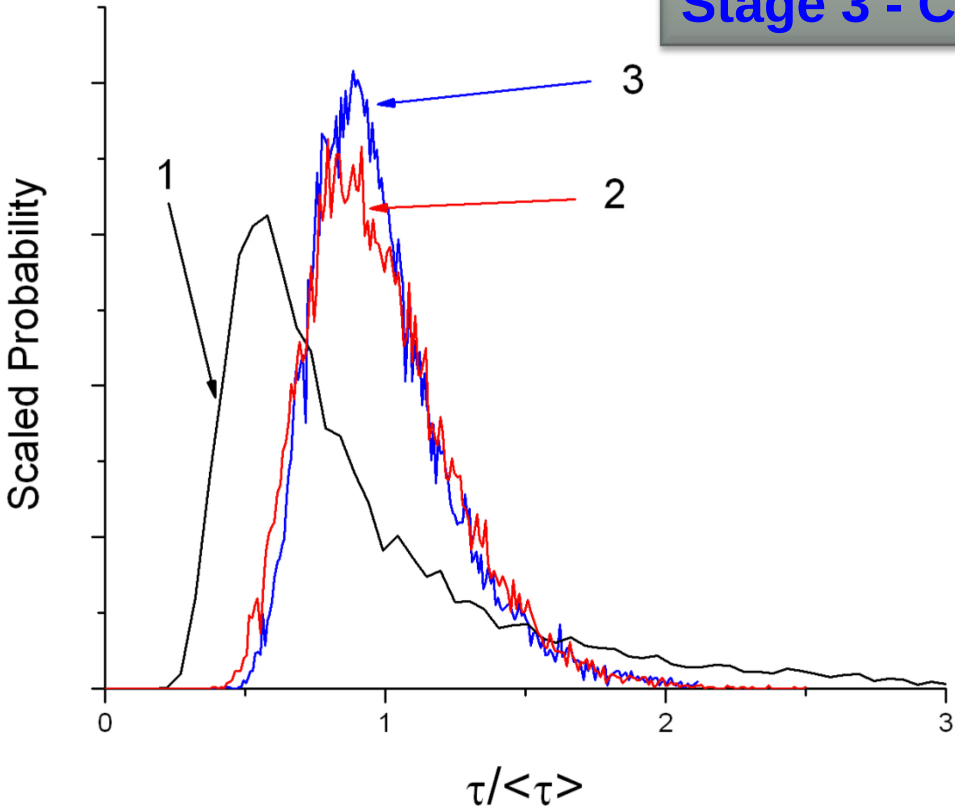
Stage 1 – Li mech

Stage 2 – CH_3OH +HO_2 updated TST

Stage 3 - CH_3OH +O_2 updated TST

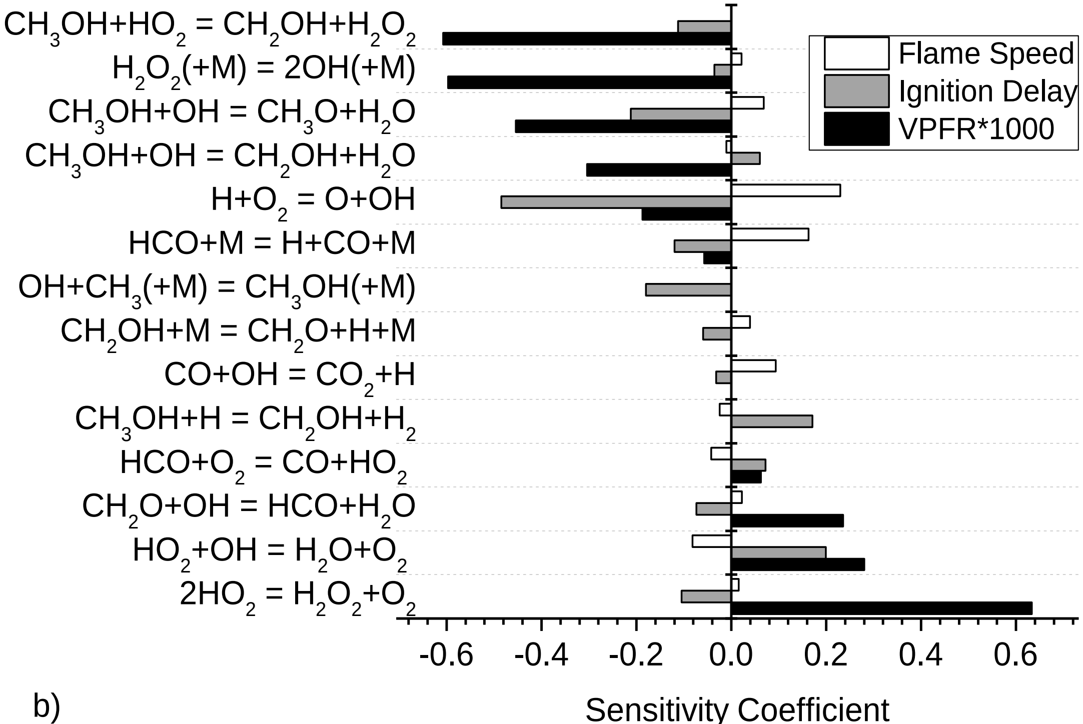
10^f ~ 2



(T,P,φ)=(1150K,5bar,1)

Further impacts?

- Modified rates from both studies are similar at low-intermediate temperatures - well constrained?
- Low sensitivity of high T shock tube simulations (Bowman 1975) and predicted flame speeds.
- High sensitivity to flow reactor data at 970 K and 2.5 atm.



b)

How to combine knowledge?

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- The reaction exhibits sensitivities for several reaction systems.
- Should start to become parameter focussed rather than mechanism/target focussed?
- Possibility to incorporate all sets of data to which a parameter is sensitive within a Bayesian framework.
- Does this get too messy for complex fuels?

Possible for H_2/O_2

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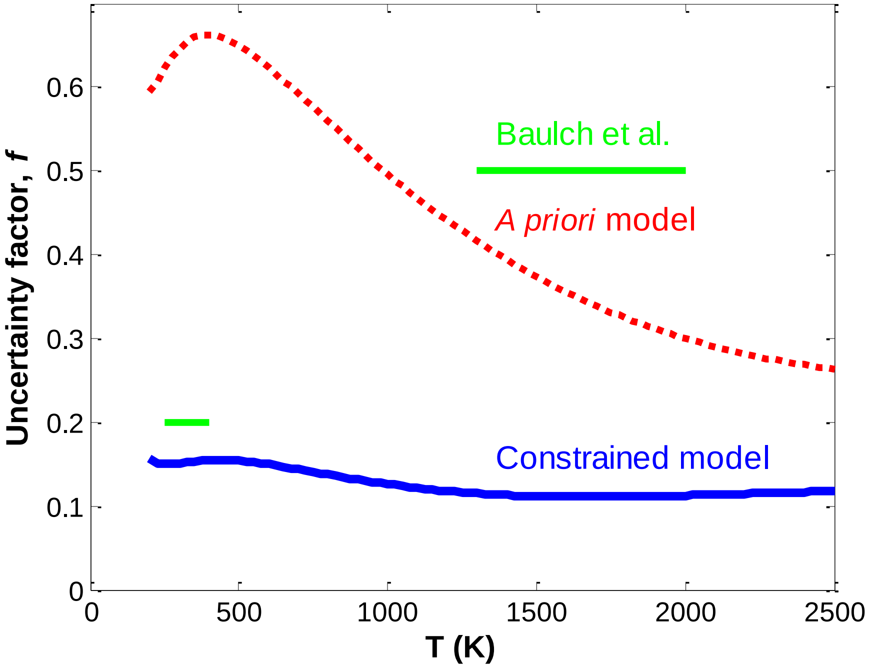
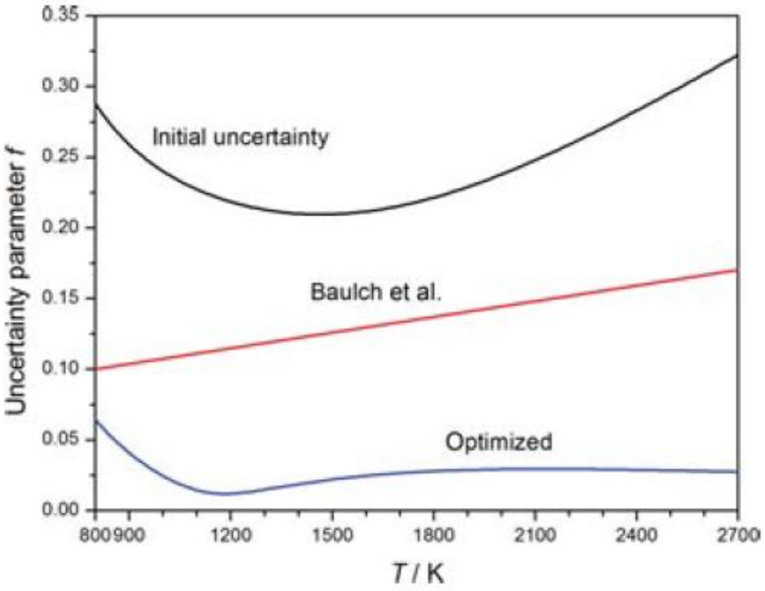


HO_2+OH=H_2O+O_2, Burke et al. 2012

Data from TST, discharge flow, shock tubes used.

$H+O_2$=OH+O, Turányi et al. 2012

Data from ignition delays, shock tubes



Larger fuels?

- Target predictions for more complex mechanisms are unlikely to be driven by only 1 or 2 parameters.
- What type of approach should be adopted?
- A hierarchical one where the simpler and better constrained systems are tackled first?
    - Turányi’s approach only selects data which is strongly sensitive to parameters being constrained i.e. reasonably well isolates parameters.
- The resulting more tightly constrained parameters could then be included in studies of more complex fuels – helping to isolate the other reactions.

Example 2: Butane oxidation in a jet stirred reactor

Performance of EXGAS mech.

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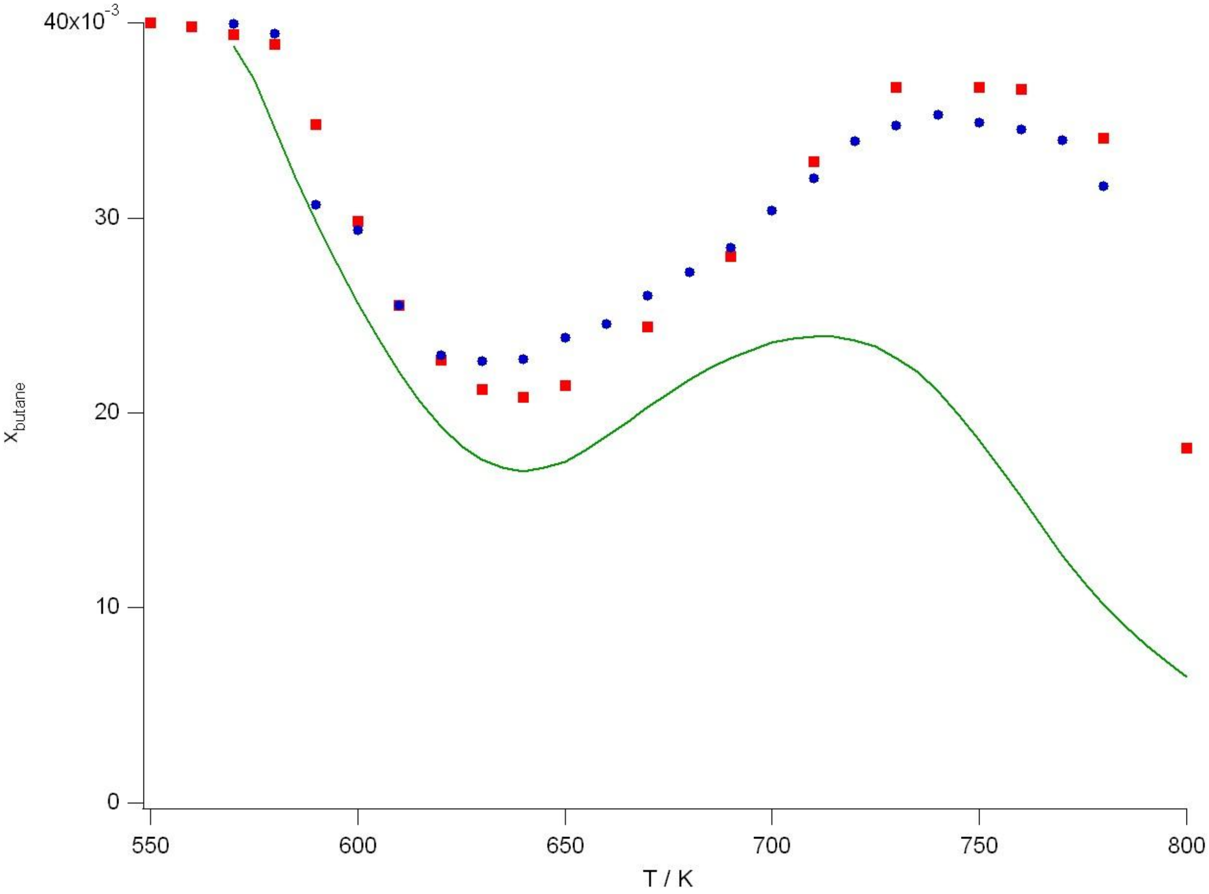
Isothermal jet-stirred reactor

1 atmosphere

Residence time : 6 s

Equivalence ratio of 1

4% butane as inlet mole fraction.



Methodology

- EXGAS mechanism - 1304 uncertain *A*-factors for forward reactions studied.
- Very large dimensional input parameter space.
- Screen out unimportant parameters before full global analysis.
- Linear sensitivities at several temperatures used for screening.
- Gives better coverage for remaining parameters allowing smaller sample size.

Global Analysis

- 31 *A*-factors selected for global runs based on the linear screening.
- Input uncertainty factors assigned from appropriate evaluation studies where available - C_0-C_2 reactions base (Baulch *et al.* 1994) .
- For calculated parameters within the primary and secondary mechanisms, $10^f \sim 3$.
- n-butane + OH $10^f \sim 0.3$ used based on (Sivaramakrishnan *et al.* 2009).

Global analysis (750 K)

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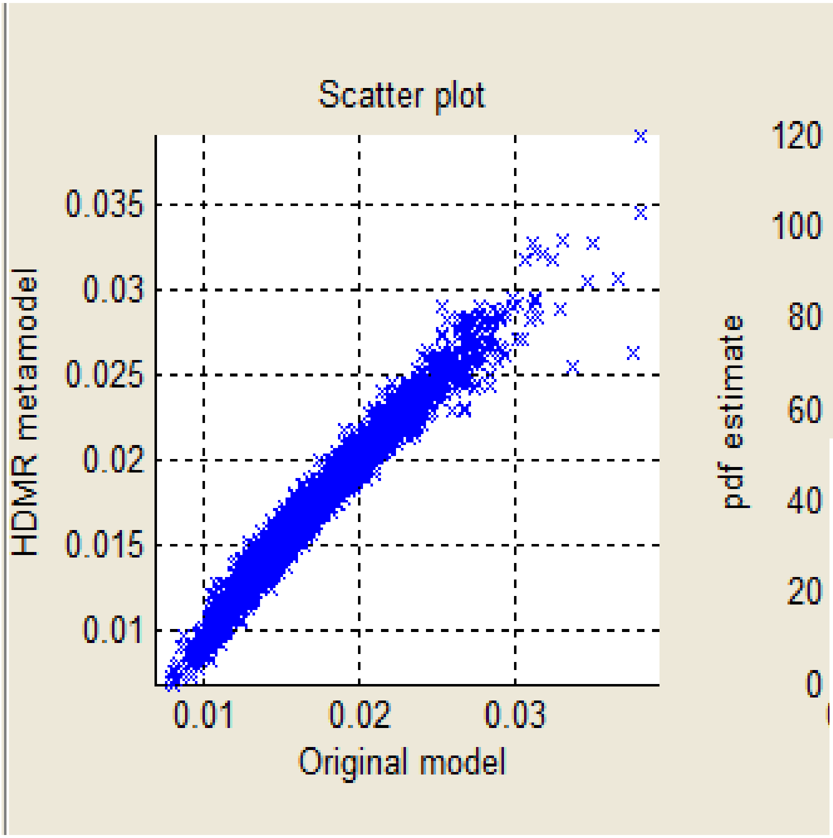

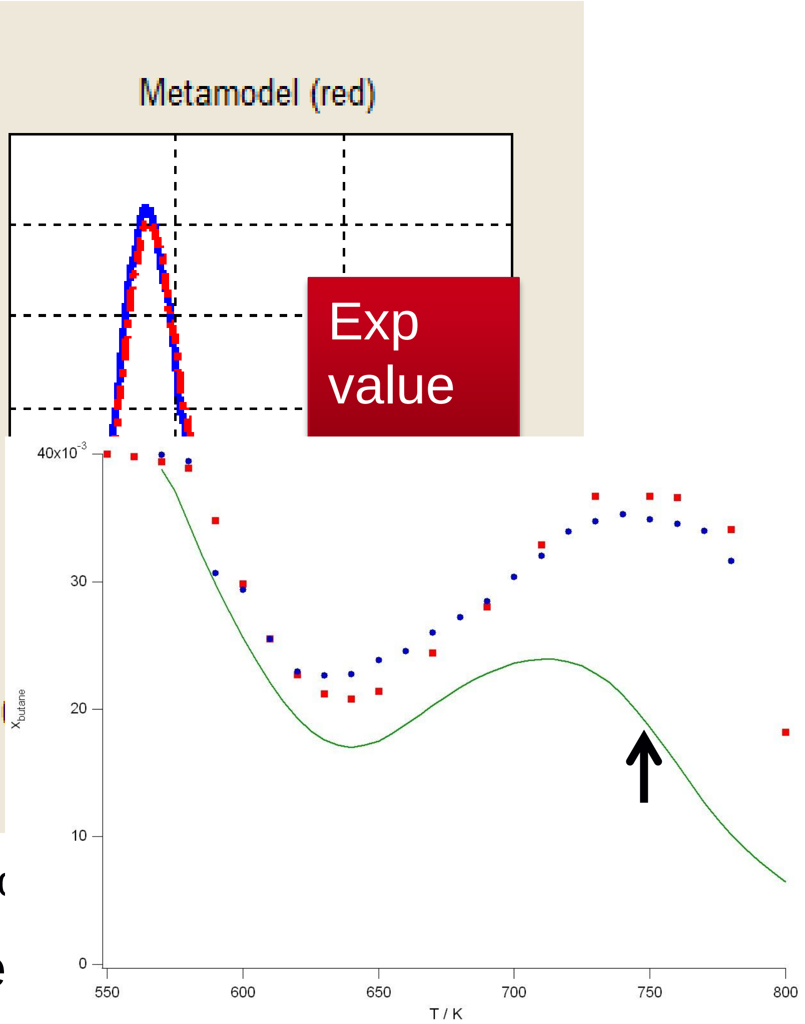

Exp value

- Wide distribution from zero to 75
- Experimental value very infreque
- Missing steps or too tight uncertainties used?

Global sensitivities: no dominant reaction

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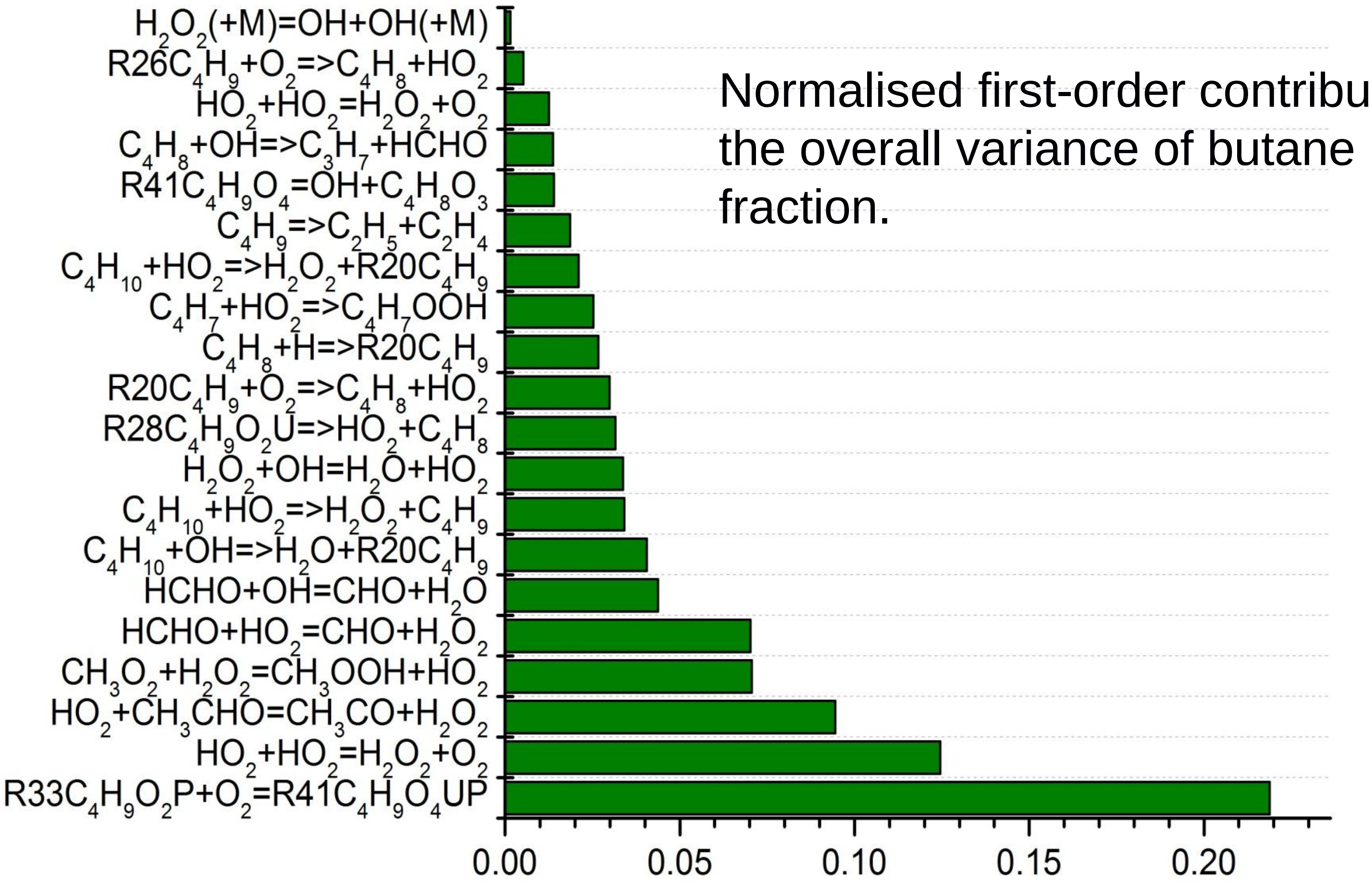
JSR (T_{res} 6 s, *P* 1 atm, stoich, 4% *n*-butane, 750 K)

Normalised first-order contributions to the overall variance of butane mole fraction.



Improving model robustness?

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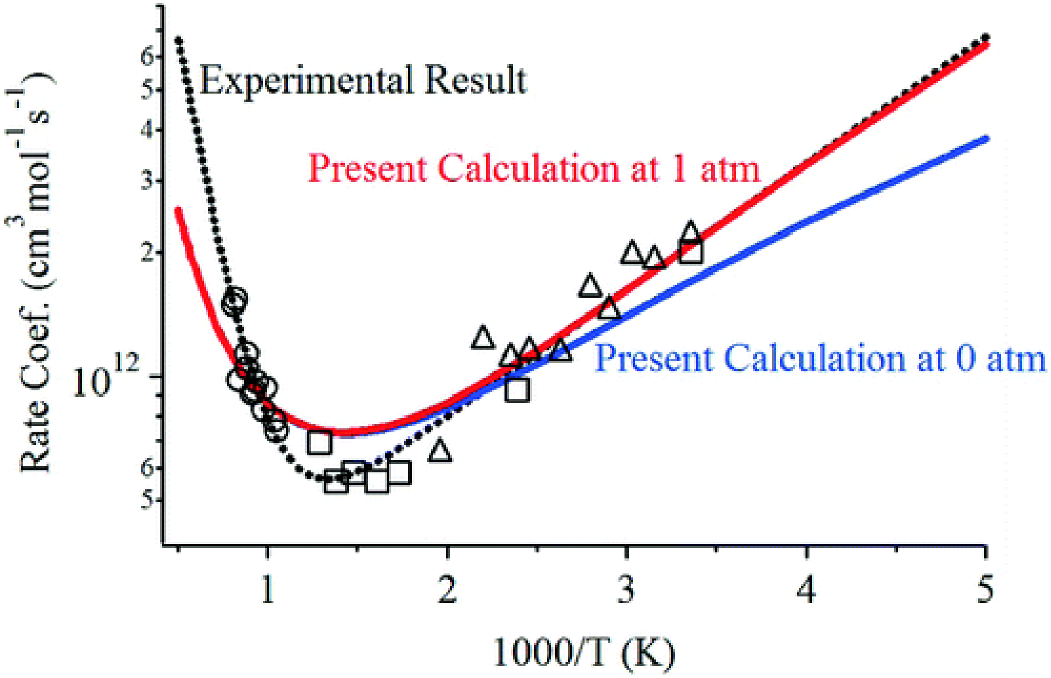
- The ntc region appears to be highly uncertain.
- Many reactions contribute to uncertainty.
- Are there missing steps or are assumptions about input uncertainties optimistic?
- Should a hierarchical Bayesian approach be adopted?
  - ➢ Start first with H_2/O_2 chemistry.
  - ➢ Then tackle HCHO reactions.
  - ➢ Then C2 chemistry.
  - ➢ Then try to constrain reactions from C4 scheme.
- What other experiments could help to constrain these important parameters and how do we find out?

HO_2+HO_2 (Zhou et al. 2012)



- TST calculations.
- Transition state ridge upward by 1 kcal/mol to better fit experiments of Patrick, Lightfoot and Kappel.
- Original f_{max} (Baulch 1994) was 0.4.
- Probably could be reduced using optimisation approaches.

Aldheydes + HO_2

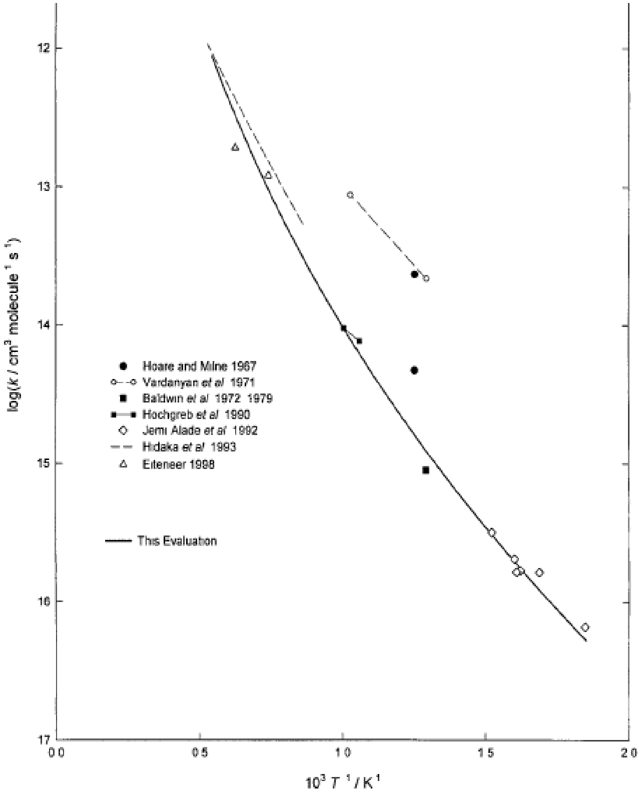
$HO_2+CH_3CHO=CH_3CO+H_2O_2$

- Baulch (2005) suggests f_{max} of 0.7.
- Based on a single set of experimental measurements from 1976 (Colket et al.).

$HO_2+HCHO=CHO+H_2O_2$

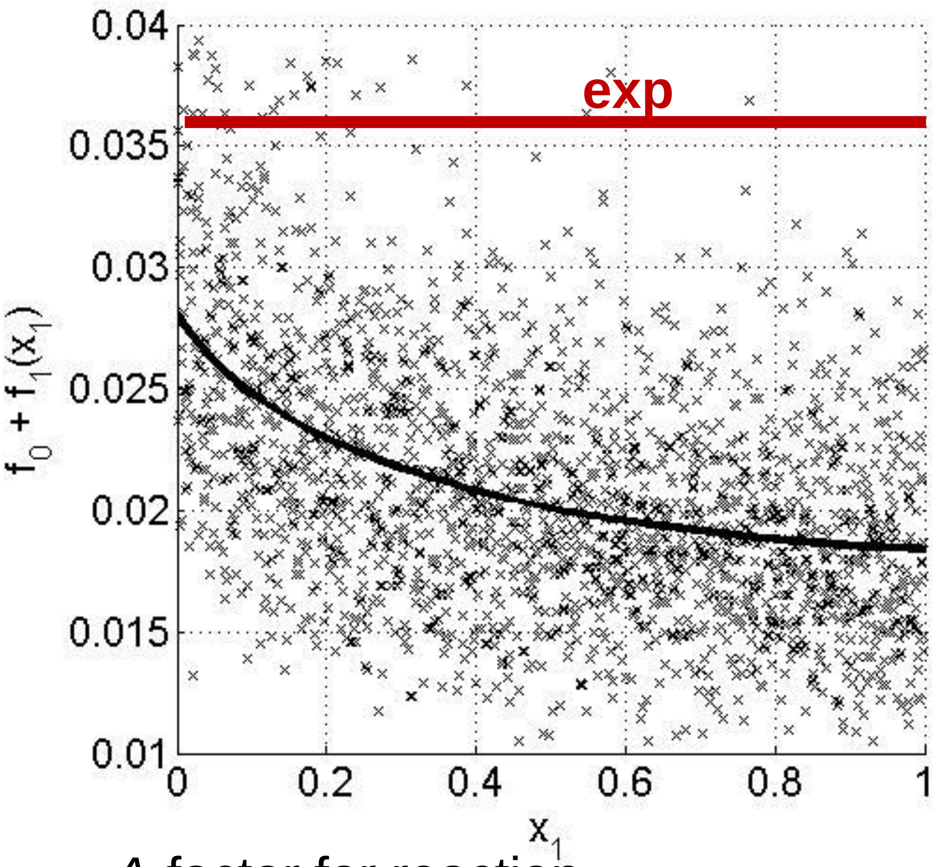
- Baulch (2005) suggests f_{max} of 0.4.
- Recent TST calcs. from Li *et al. 2005*
- Combined analysis?

What new sets of data could help to constrain these parameters better?



2^{nd} oxygen addition reactions to form O2QOOH

UNIVERSITY OF LEEDS



A-factor for reaction $R33C_4H_9O_2P+O_2=R41C_4H_9O_4UP$

- Very scattered response but data hints that rate is might be lower than the nominal value used which was based on analogy to rate coefficients for propyl + O_2 from De Sain et al. (2003)
- Clearly a key reaction class driving fuel reactivity.
- $QOOH+O_2$ studied for propane and pentane theoretically by Bozzelli and Coworkers but not for butane.

2nd oxygen addition reactions to form O2QOOH

- Rate used was estimated on the basis of analogy to rate coefficients for propyl + O_2 from De Sain et al. (2003)
- Recent theoretical calculations exist from Goldsmith et al. (2012) for the propyl + O_2 system suggest that for the main channel the reaction forming O2QOOH is slower than the equivalent rate for propyl + O_2 at 750 K.
- An equivalent temperature dependant study for butyl would be very useful.
- Still large uncertainties for these types of reactions.
- If basic C1/H scheme was better constrained then then indirect experiments might help to constrain rates for reactions which are difficult to study experimentally.

Forward steps

- Could be useful to collate information about conditions over which certain reactions have high sensitivity coefficients.

  i.e. parameter focus rather than experimental.

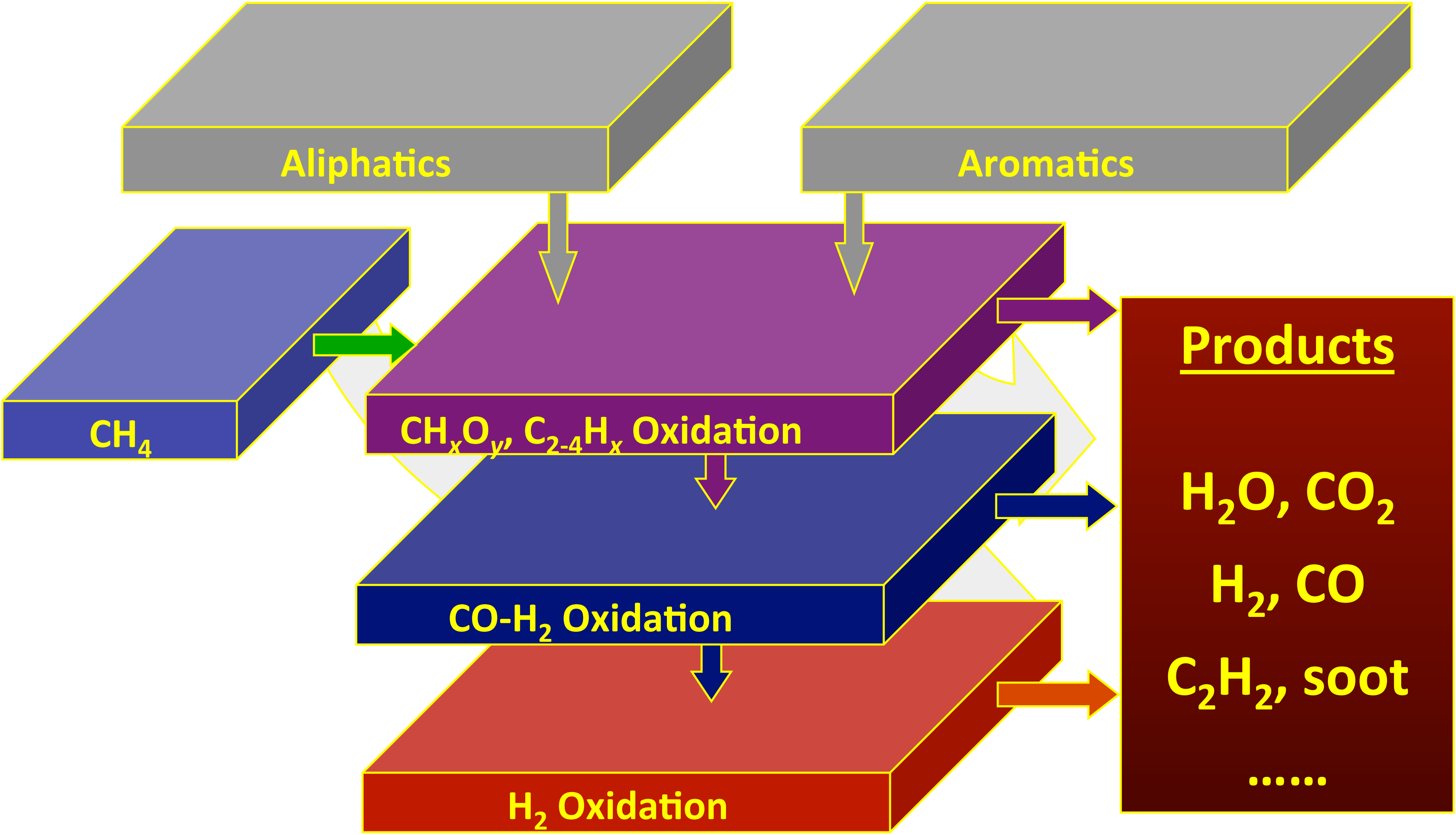
- Would involve simulating a lot of data sets over different temperatures and pressures for a lot of different fuels in a consistent way.
- Optimisation approaches which combine data sets are clearly a way forward in terms of reducing input uncertainty distributions.
- Possible for H_2/O_2 chemistry (last talk).
- How to do it for complex fuels raises all sorts of questions.

Towards a predictive combustion chemistry model – Uncertainty propagation and minimization

Hai Wang and David A. Sheen

University of Southern California, Los Angeles, California, USA

Model Hierarchy



Aliphatics

Aromatics

CH_4

CH_xO_y, $C_{2\text{-}4}H_x$ Oxidation

CO-H_2 Oxidation

H_2 Oxidation

Products

H_2O, CO_2

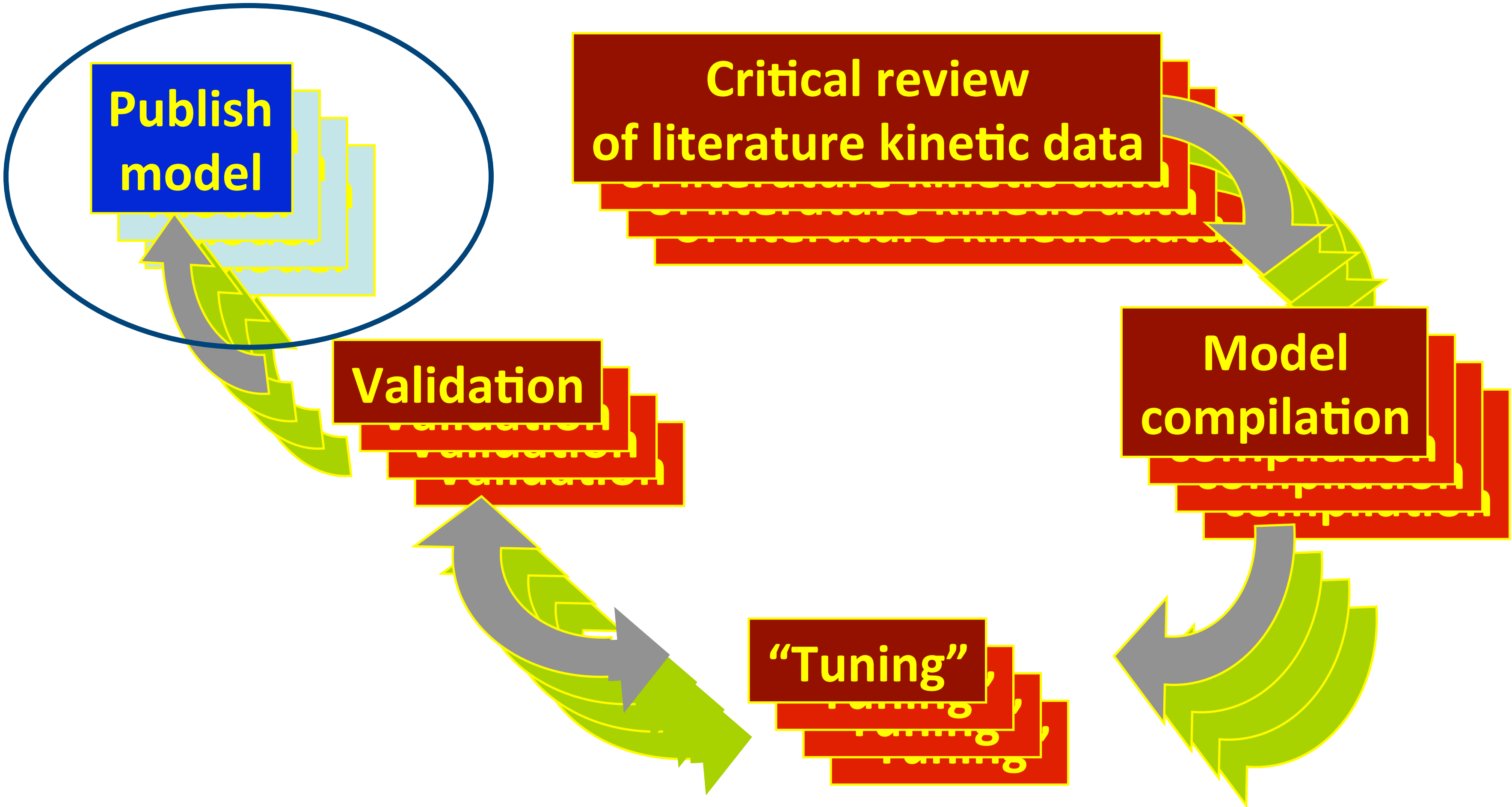
H_2, CO

C_2H_2, soot

……

Reaction Model Development

The Current Approach



proliferation of models

Publish model

Critical review of literature kinetic data

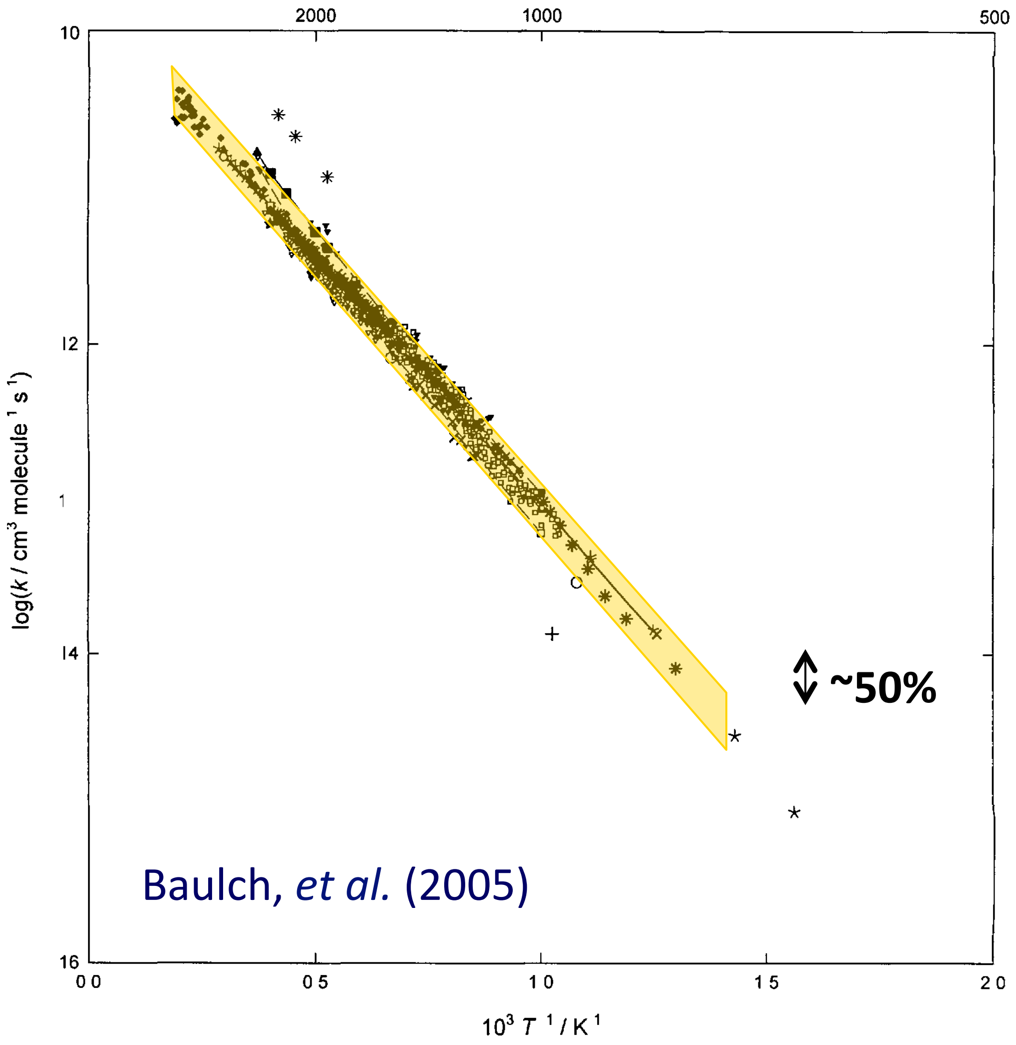
Model compilation

"Tuning"

Validation

Kinetic Rate Parameter Uncertainties

$H + O_2 \leftrightarrow OH + O$ (R1)

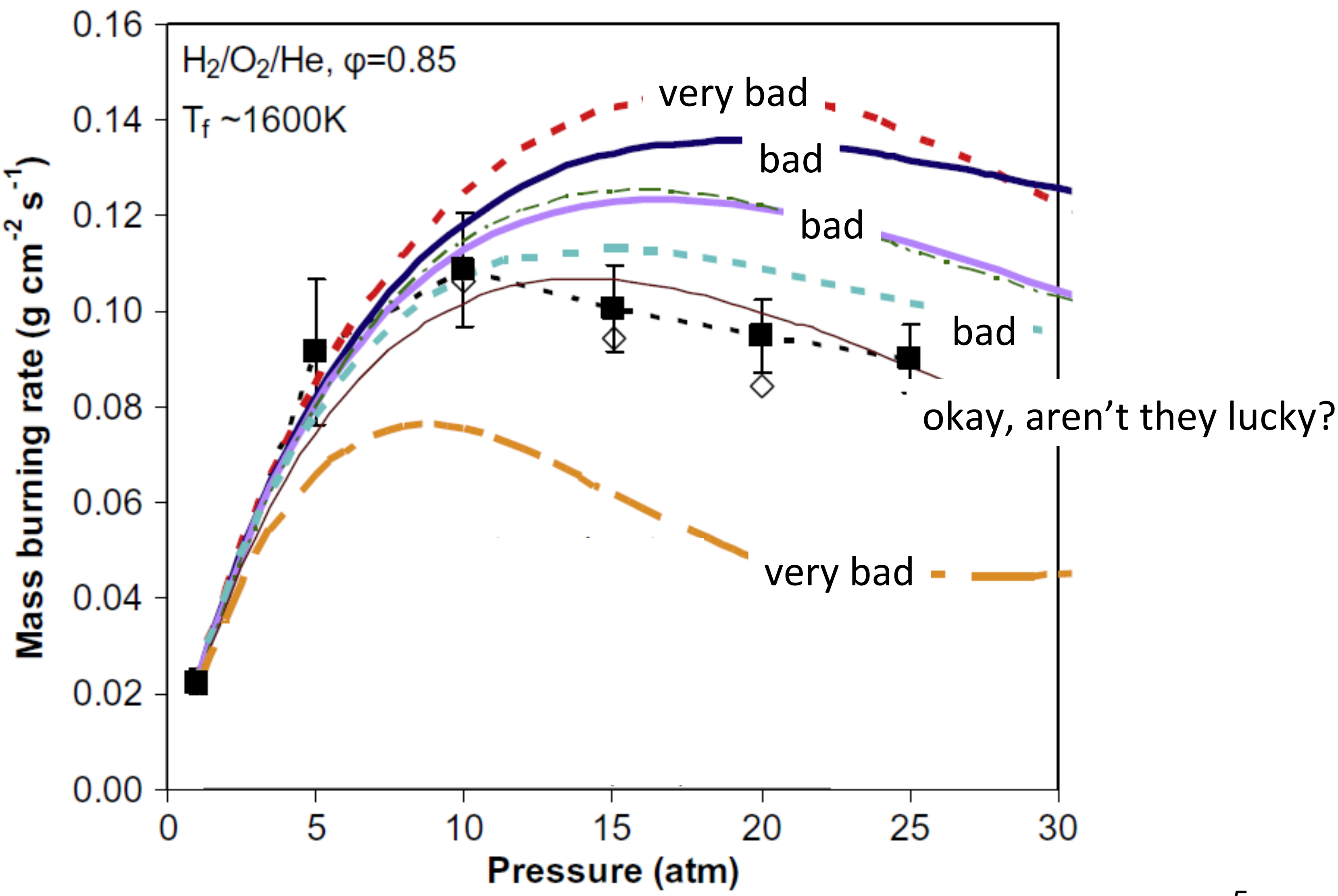


↕ ~50%

Baulch, *et al.* (2005)

- Uncertainty factor ~1.25
- Logarithmic sensitivity coefficient = 0.24 (ethylene-air, *f* = 1, *p* = 1 atm)
- ±5% (±4 cm/s) uncertainty in predicted flame speed due to R1 alone
- Key question: How do we propagate uncertainties in rate constants in combustion simulations?

Uncertainty Uncertainty Uncertainty Uncertainty Uncertainty Uncertainty



very bad

bad

bad

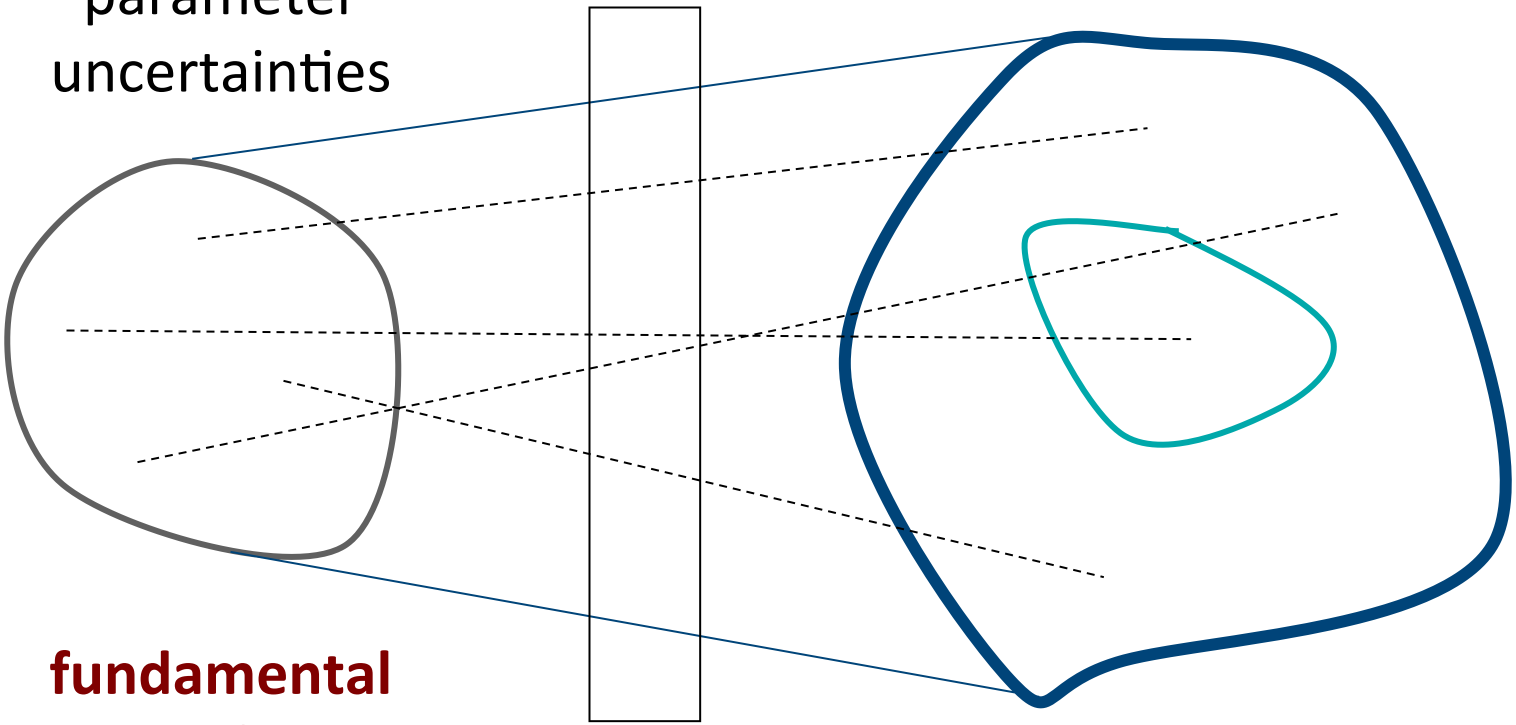
bad

okay, aren’t they lucky?

very bad

Burke, *et al.* (2010)

Uncertainty Uncertainty Uncertainty Uncertainty Uncertainty Uncertainty



rate parameter uncertainties

Physical problem

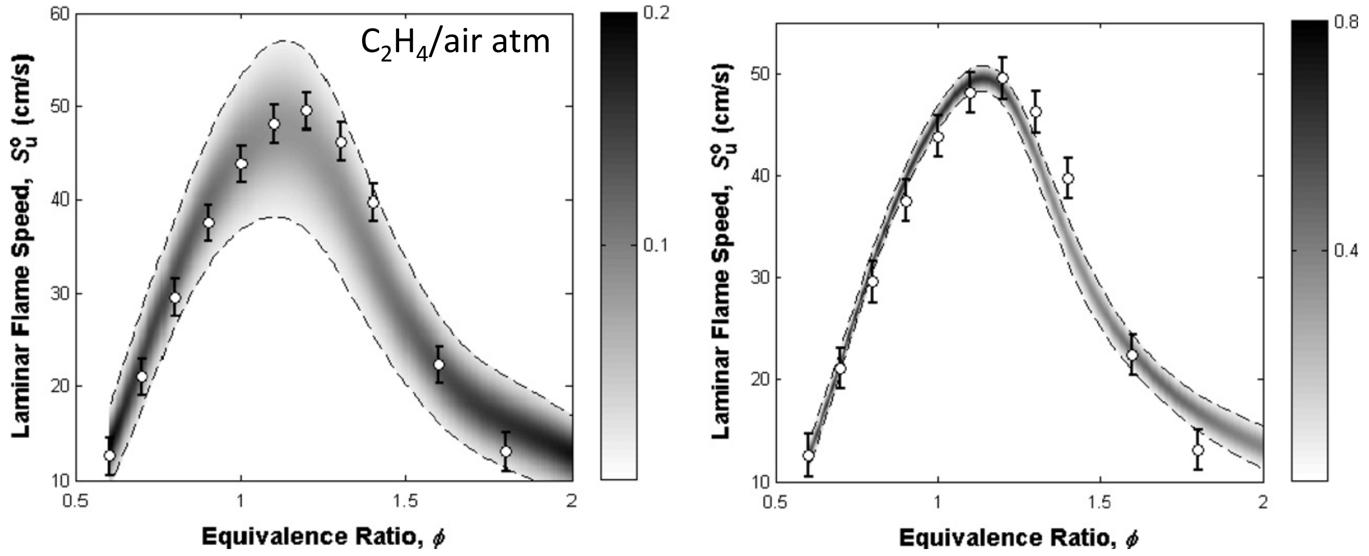
data uncertainty

fundamental reaction kinetics expt + calc

fundamental combustion expt.

MUM-PCE

- Method of Uncertainty Minimization – Polynomial Chaos Expansions
  - Mathematical foundation and numerical methods: Sheen & Wang “Kinetic uncertainty quantification and minimization using polynomial chaos expansions,” *Combustion and Flame*, DOI:10.1016/j.combustflame.2011.05.010.



  - Model prediction presented as a (2-*s*) band of uncertainty resulting from kinetic parameter uncertainties.
  - Model uncertainty may be constrained by experimental data (ignition delay, species-time history, flame speeds etc)

MUM-PCE: Methods

- **Stochastic Spectral Expansion:** express kinetic parameter *x_i* as a polynomial expansion of basis random variables

$$x_i = x_i^{(0)} + \sum_{j=1}^{m} \alpha_{ij}\xi_j + \sum_{k=1}^{m}\sum_{j=k}^{m} \beta_{ijk}\xi_j\xi_k + \ldots$$

Following N. Wiener (1938), D.B. Xiu, *et al.* (2002)

- **Solution Mapping**: use polynomial response surface to express the relation between a combustion response *h* and **x**

$$\eta_r(\mathbf{x}) \cong \eta_{r,0} + \sum_{i=1}^{N} a_{r,i}x_i + \sum_{i=1}^{N}\sum_{j\geq i}^{N} b_{r,ij}x_i x_j$$

Forward Uncertainty Propagation

$$\eta_r(\mathbf{x}) = \eta_{r,0} + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} \sum_{j \geq i}^{n} b_{ij} x_i x_j$$

Response surface from solution mapping

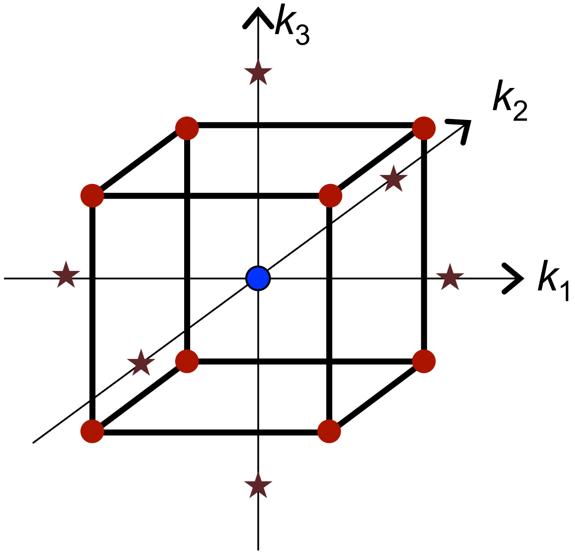
$$x_i = \tfrac{1}{2} \xi_i$$

Spectral representation of uncertainty in x's
(mean = 0, s = 0.5, each indep't of others)

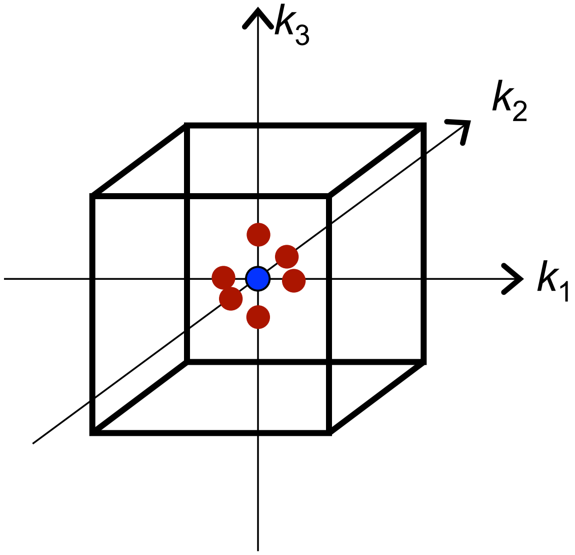
$$\eta_r(\mathbf{x}, \boldsymbol{\xi}) = \eta_r\left(\mathbf{x}^{(0)}\right) + \sum_{i=1}^{M} \hat{\alpha}_{r,i} \xi_i + \sum_{i=1}^{M} \sum_{j=i}^{M} \hat{\beta}_{r,ij} \xi_i \xi_j$$

Solution Mapping Method

- **Fit a response surface to the model**



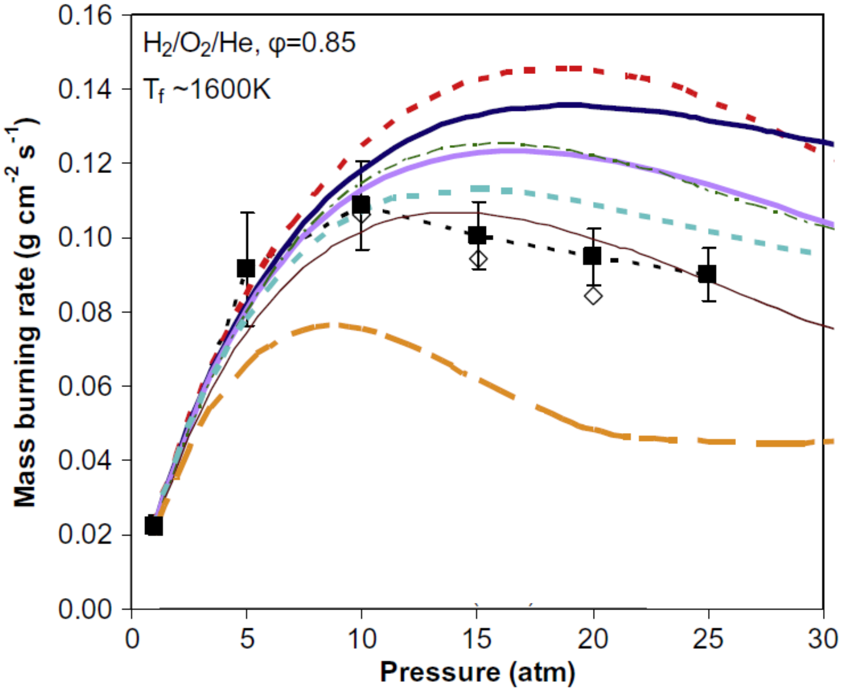
Central-Composite Factorial Design

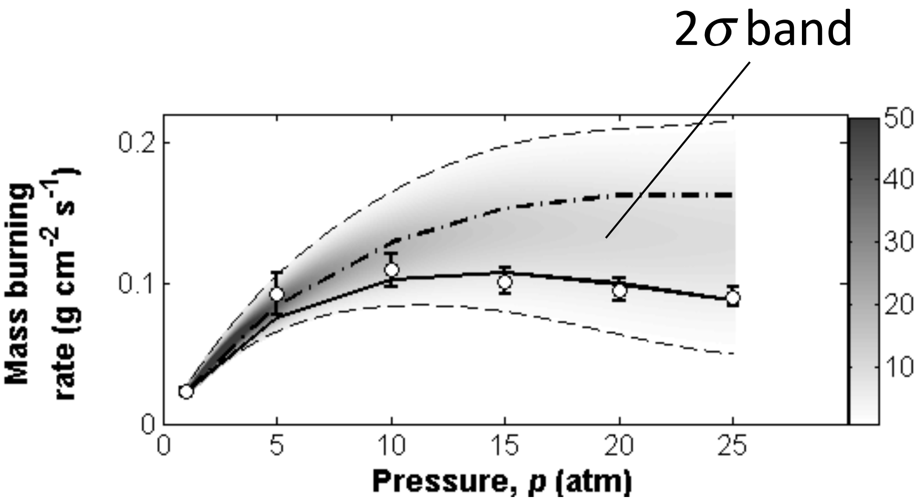


Sensitivity Analysis Based Design

G.E.P. Box, *et al.* (1978), Frenklach *et al*. (1992), S.G. Davis *et al.* (2004)

MUM-PCE – Application in H_2/O_2 Combustion





- High-pressure data sensitize kinetics of hydrogen oxidation.
- A large number of models outside experimental uncertainty at high pressures.

Burke, *et al.* (2010)

- 2σ uncertainty band calculated by MUM-PCE, based on rate parameter uncertainties.
- Models are statistical samples of parameter uncertainties.

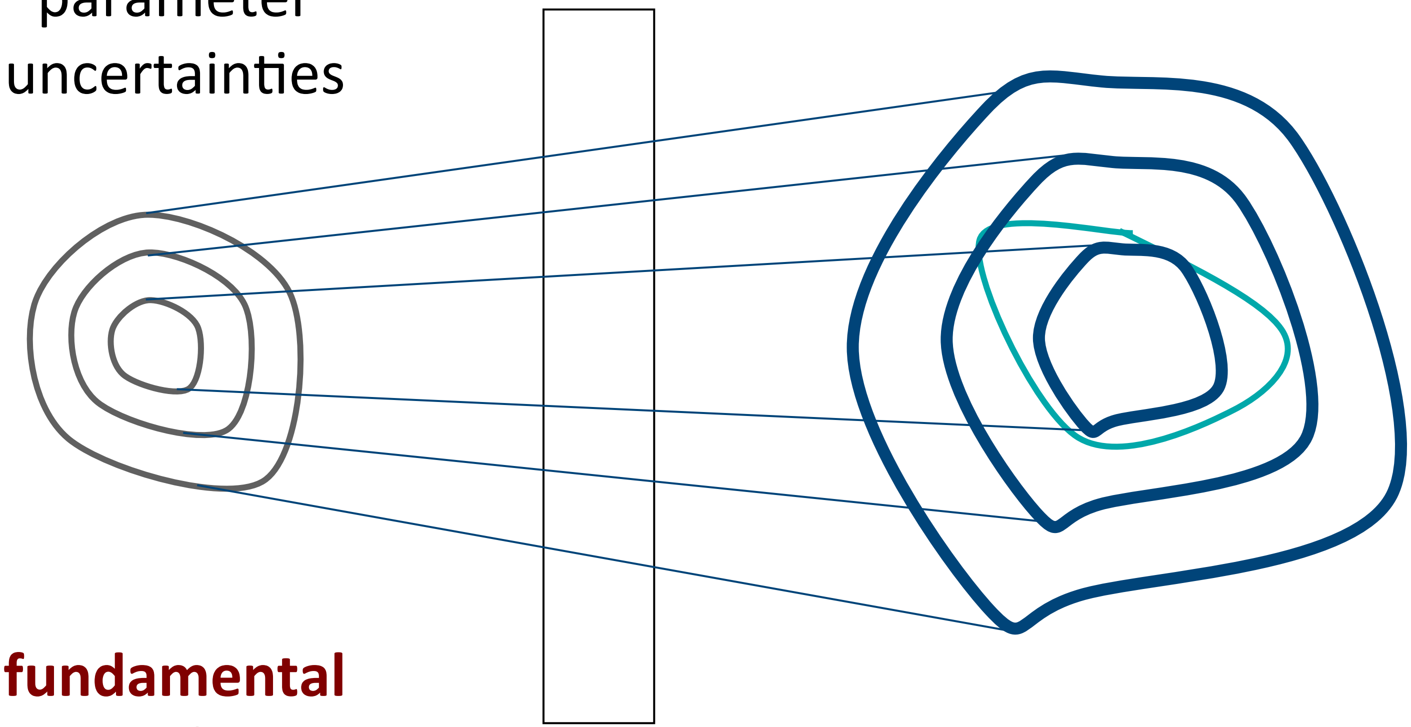
Sheen & Wang (2011)

Uncertainty Uncertainty Uncertainty Uncertainty Uncertainty Uncertainty

rate parameter uncertainties

Physical problem

data uncertainty



fundamental reaction kinetics expt + calc

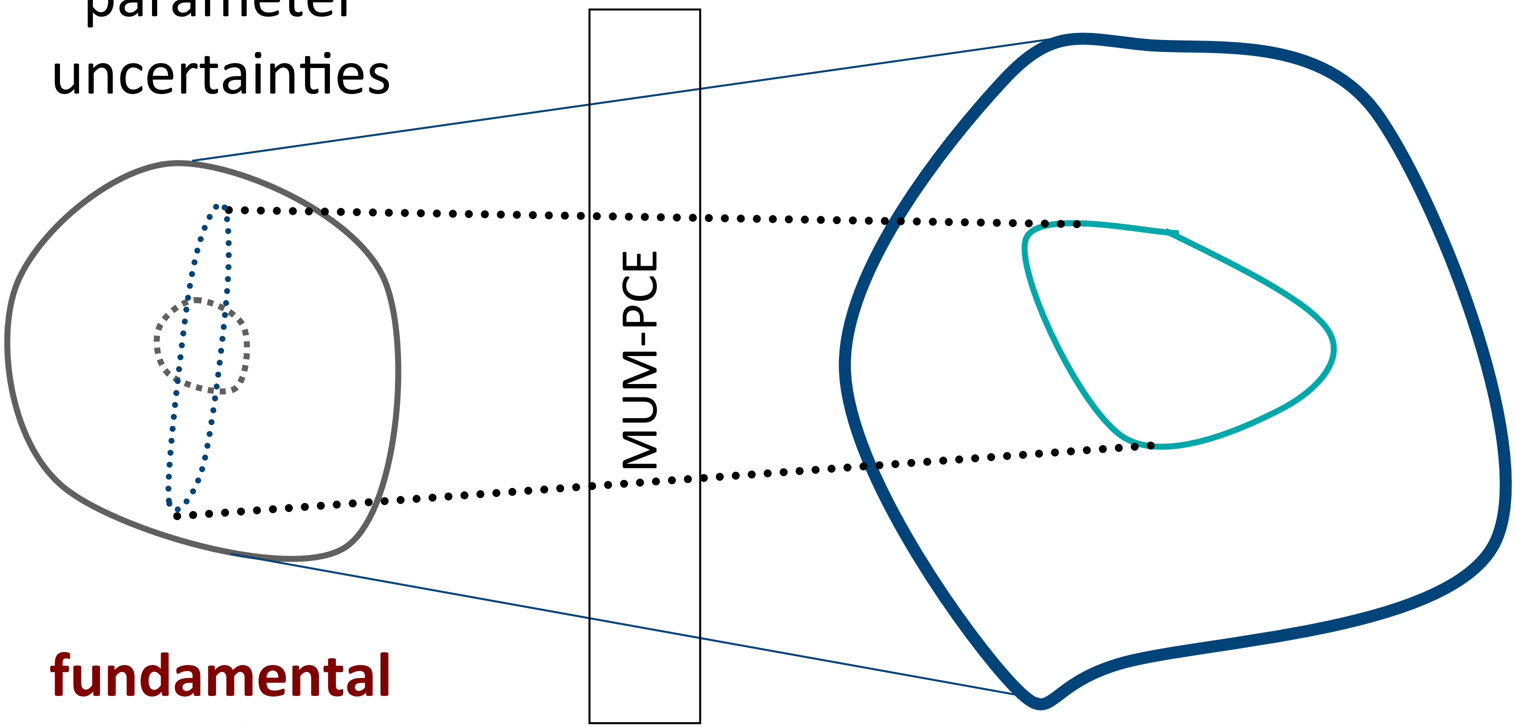
fundamental combustion expt.

MUM-PCE

rate
parameter
uncertainties

Physical
problem

data
uncertainty



**fundamental
reaction kinetics
expt + calc**

**fundamental
combustion expt.**

Method of Uncertainty Minimization

$$\mathbf{x} = \mathbf{x}_0 + \boldsymbol{\alpha}\boldsymbol{\xi}$$

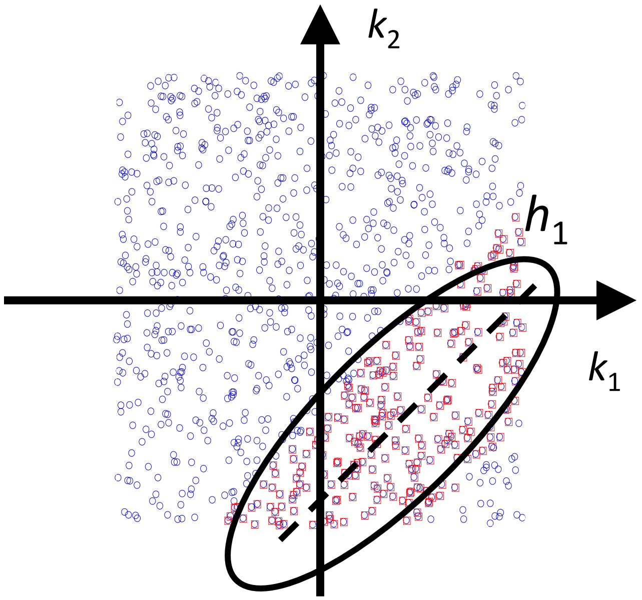
Chemical model
+ associated uncertainty

$$\eta_r(\mathbf{x}) \cong \eta_{r,0} + \sum_{i=1}^{N} a_{r,i} x_i + \sum_{i=1}^{N} \sum_{j \geq i}^{N} b_{r,ij} x_i x_j$$

Physics model

$$\eta_r(\mathbf{x}, \boldsymbol{\xi}) = \eta_r\left(\mathbf{x}^{(0)}\right) + \sum_{i=1}^{m} \hat{\alpha}_{r,i} \xi_i + \sum_{i=1}^{m} \sum_{j=i}^{m} \hat{\beta}_{r,ij} \xi_i \xi_j$$

Predictions
+ associated uncertainty



$$\Phi\left(\mathbf{x}_0^*\right) = \min_{\mathbf{x}_0} \left\{ \sum_{r=1}^{M} \frac{\left[\eta_{r,0}^{\text{obs}} - \eta_r(\mathbf{x}_0)\right]^2}{\left(\sigma_r^{\text{obs}}\right)^2} + \sum_{n=1}^{N} \frac{\left(x_{0,n}\right)^2}{\left(\sigma_n\right)^2} \right\}$$

$$\Sigma = \left[\sum_{r=1}^{n} \frac{1}{\left(\sigma_r^{\text{obs}}\right)^2} \left(\mathbf{b}\mathbf{x}_0^* \mathbf{x}_0^{*T} \mathbf{b} + \mathbf{a}\mathbf{x}_0^{*T} \mathbf{b} + \mathbf{b}^T \mathbf{x}_0^* \mathbf{a}^T + \mathbf{a}\mathbf{a}^T \right) + 4\mathbf{I} \right]^{-1}$$

$$\boldsymbol{\alpha}^* = \Sigma^{1/2}$$

MUM-PCE – Application in H_2/O_2 Combustion

- Model uncertainty constraining
- JetSurF 2.0 H2/CO submodel
  - 14 species, 41 reactions

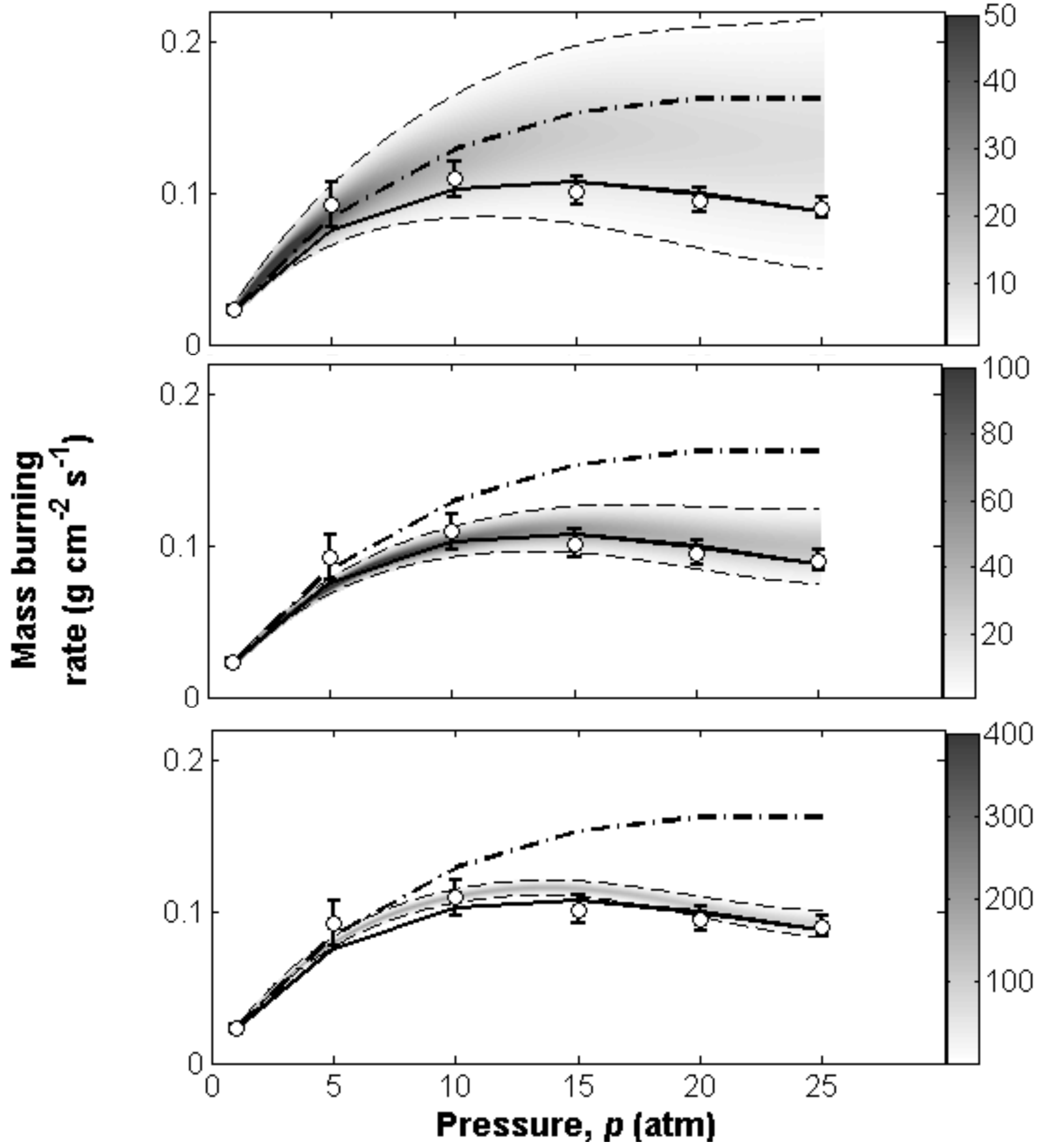
Dataset 1: From Davis, *et al.* (2005):

	No.	P_0, P_5 (atm)	T_0, T_5 (K)	f
Laminar Flame Speeds	12	1-15	298	1.0-3.0
Ignition Delay Times	13	0.5-33	1000-2600	1.0-6.1
Flow Reactor Profiles	9	1.0-16	915-1040	0.3-1.0
Laminar Flame Profiles	2	0.047	400	1.9

Dataset 2:

From Burke, *et al.* (2010):	No.	P_0, P_5 (atm)	T_0, T_5 (K)	f
Laminar Flame Speeds	18	15-25	298	0.85-2.5

MUM-PCE – Application in H_2/O_2 Combustion



Considering no experiments

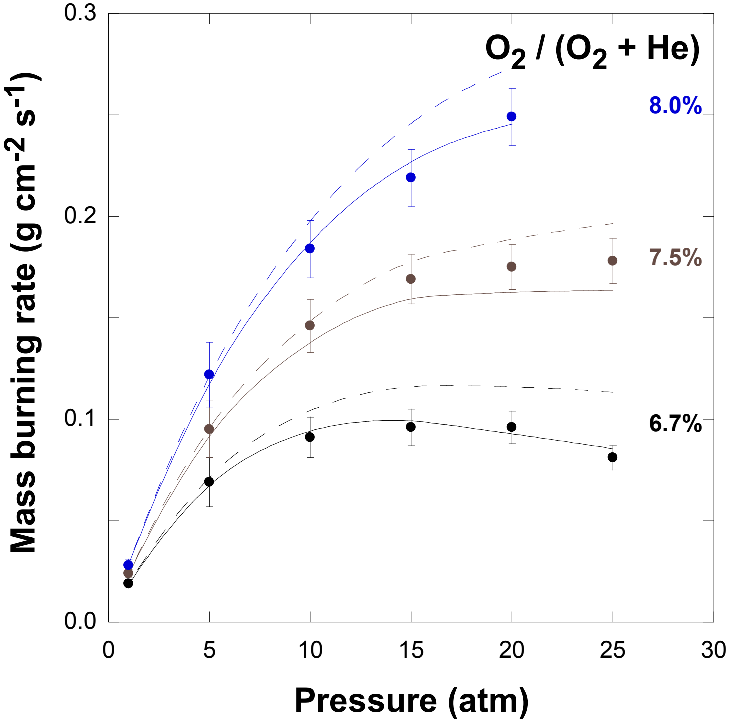
Dataset 1 (knowledge prior to 2010)

Dataset 1+2 (latest knowledge)

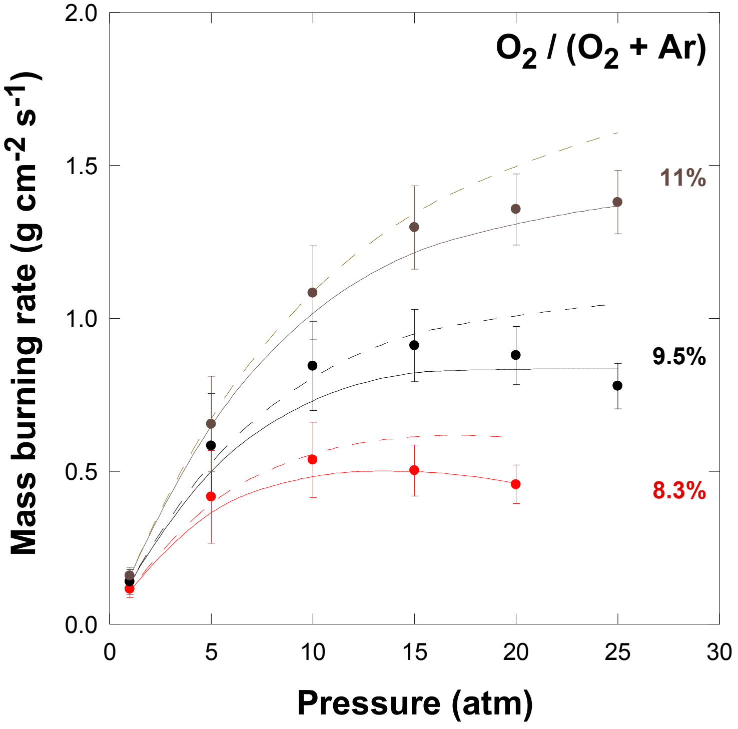
Sheen & Wang (2011)

MUM-PCE – Application in H_2/O_2 Combustion

$H_2/O_2/He$ mixtures at equivalence ratio 1



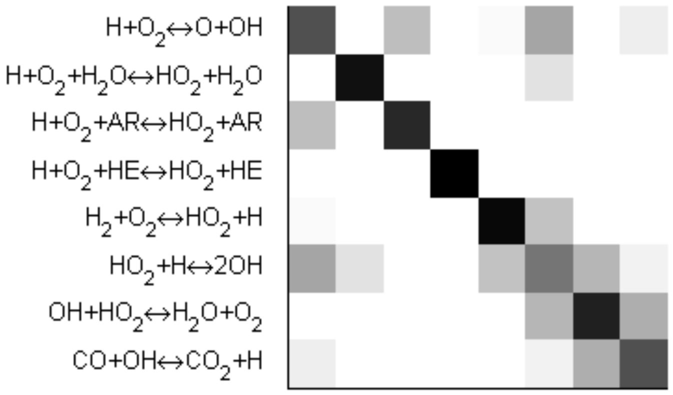
$H_2/O_2/Ar$ mixtures at equivalence ratio 2.5



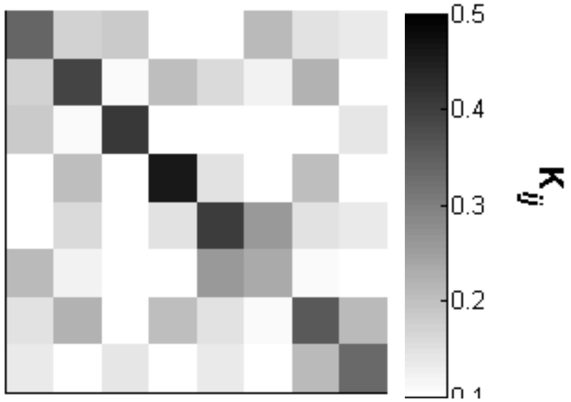
Sheen & Wang (2011)

MUM-PCE – Application in H_2/O_2 Combustion

Dataset 1
Knowledge prior to 2010

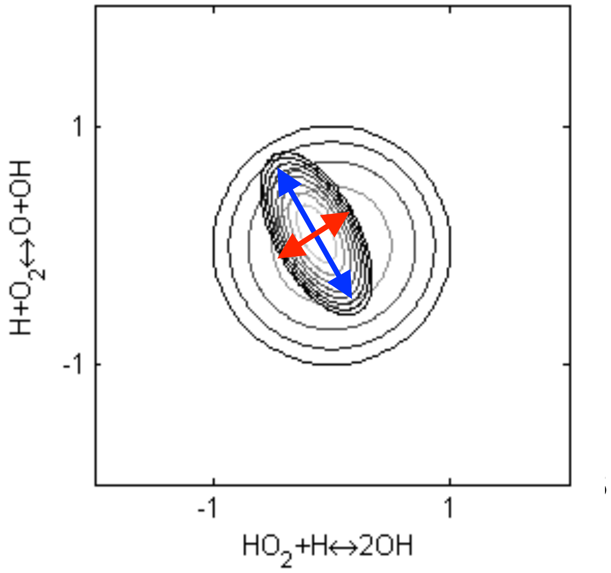


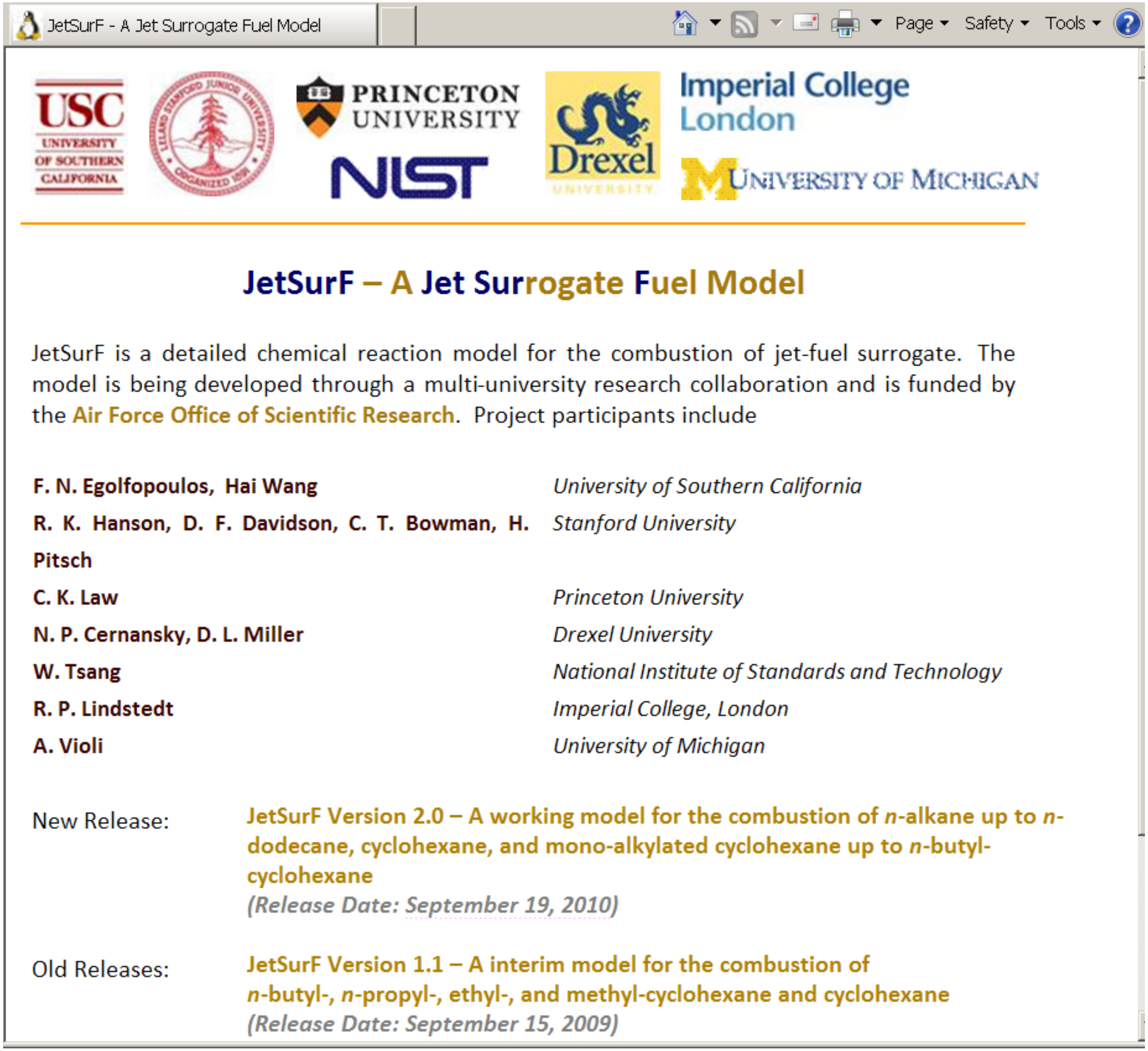
+ Burke, *et al.* (2010)
Current knowledge



Weak constraint by experiments

Strong constraint by experiments




JetSurF - A Jet Surrogate Fuel Model
Page
Safety
Tools
USC University of Southern California
Princeton University
NIST
Drexel University
Imperial College London
University of Michigan

JetSurF – A Jet Surrogate Fuel Model

JetSurF is a detailed chemical reaction model for the combustion of jet-fuel surrogate. The model is being developed through a multi-university research collaboration and is funded by the Air Force Office of Scientific Research. Project participants include

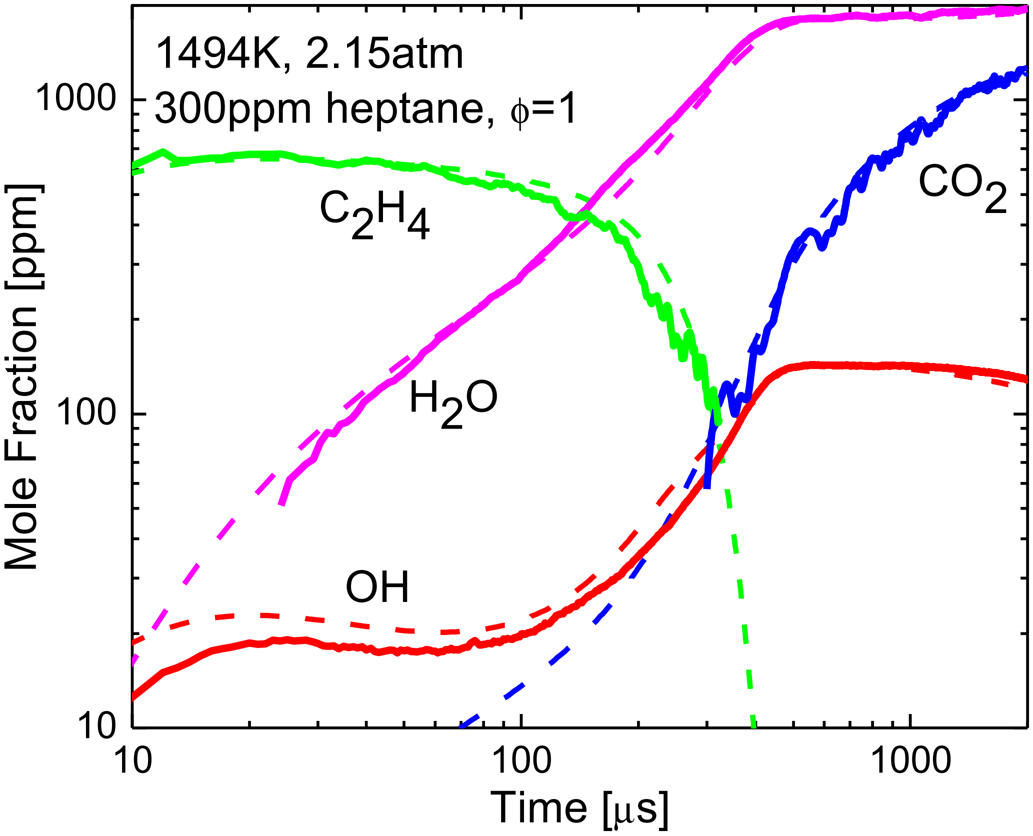
F. N. Egolfopoulos, Hai Wang	*University of Southern California*
R. K. Hanson, D. F. Davidson, C. T. Bowman, H. Pitsch	*Stanford University*
C. K. Law	*Princeton University*
N. P. Cernansky, D. L. Miller	*Drexel University*
W. Tsang	*National Institute of Standards and Technology*
R. P. Lindstedt	*Imperial College, London*
A. Violi	*University of Michigan*

New Release: **JetSurF Version 2.0 – A working model for the combustion of *n*-alkane up to *n*-dodecane, cyclohexane, and mono-alkylated cyclohexane up to *n*-butyl-cyclohexane**
(Release Date: September 19, 2010)

Old Releases: **JetSurF Version 1.1 – A interim model for the combustion of *n*-butyl-, *n*-propyl-, ethyl-, and methyl-cyclohexane and cyclohexane**
(Release Date: September 15, 2009)

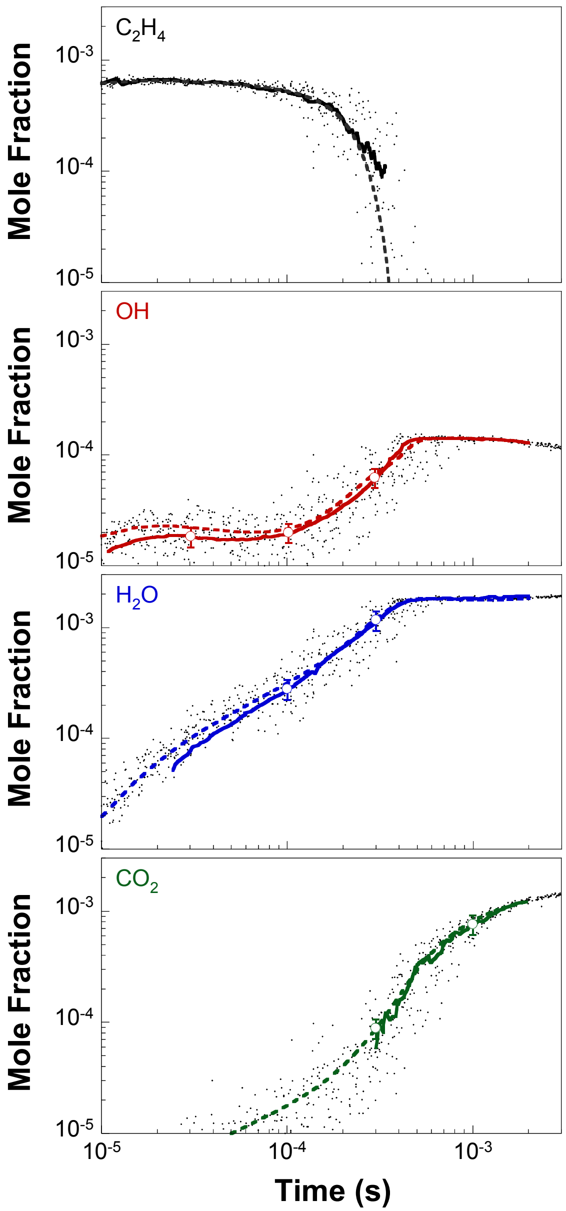
JetSurF Validation – Species Concentrations behind reflected shock waves

B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, F. N. Egolfopoulos, H. Wang, S. S. Vasu, D. F. Davidson, R. K. Hanson, H. Pitsch, C. T. Bowman, A. Kelley, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, A. Violi, R. P. Lindstedt, A high-temperature chemical kinetic model of n-alkane oxidation, JetSurF version 1.0, September 15, 2009 (http://melchior.usc.edu/JetSurF/Version1_0/Index.html).



Plot stolen from Ron Hanson. Solid line: experiments; dashed line: JetSurF

Prediction Uncertainties in As-Compiled Model



Good nominal prediction with significant uncertainty!

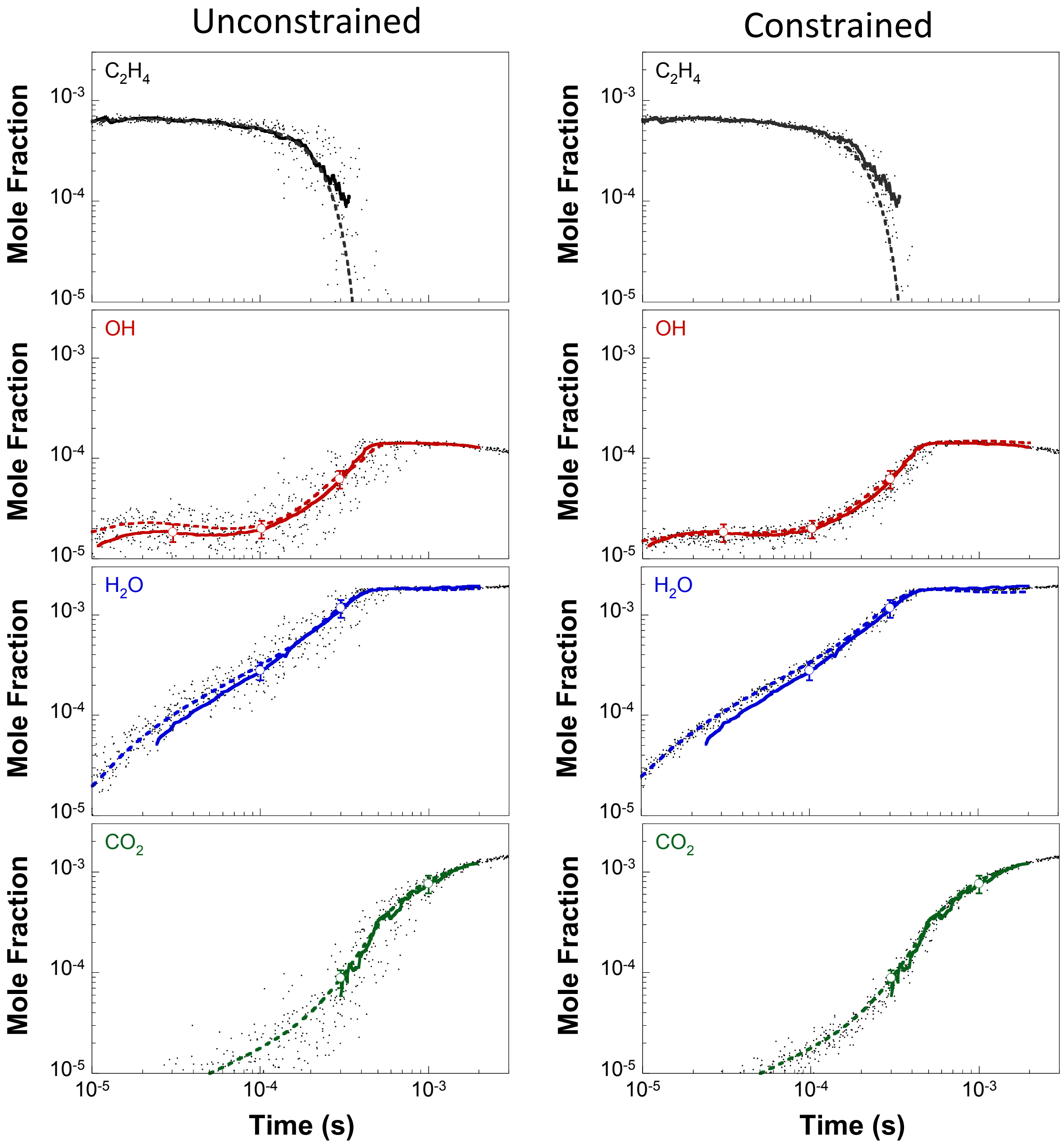
Chemistry Model & Experimental Targets

- Modified JetSurF 1.0
  - 196 species, 1478 reactions

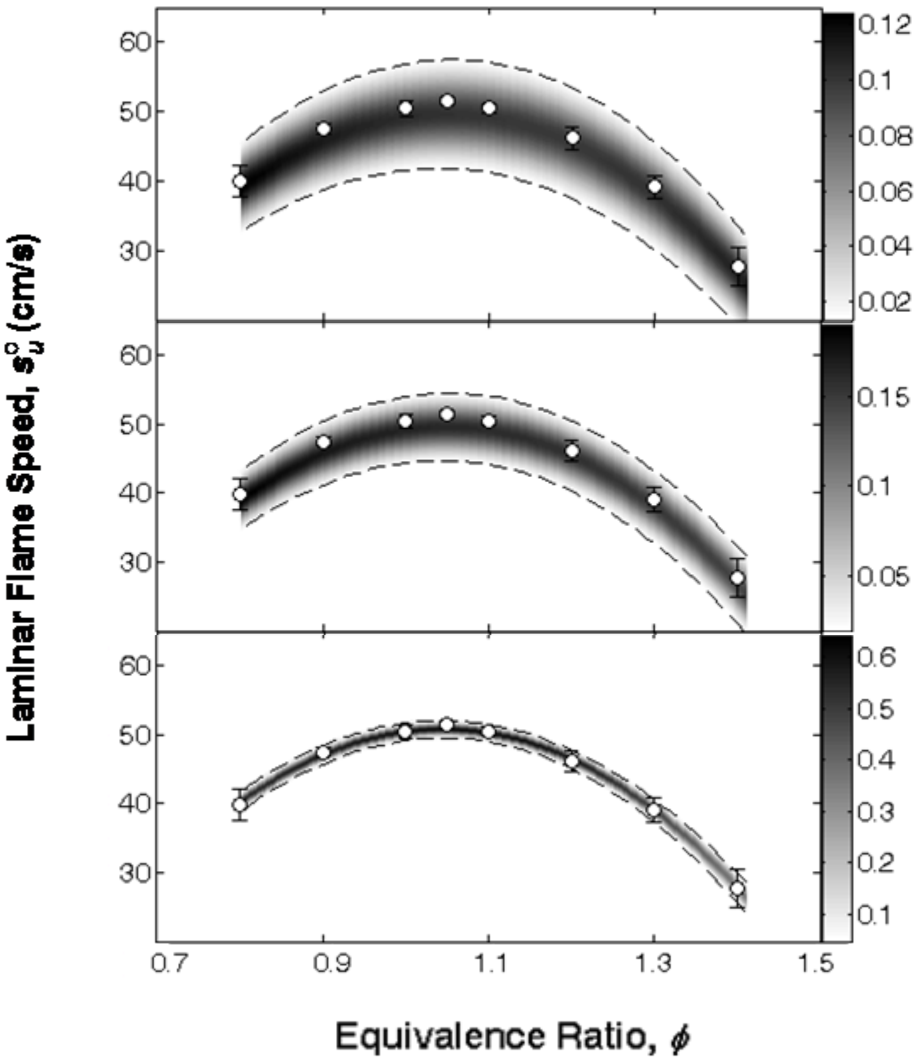
	No.	P_0, P_5 (atm)	T_0, T_5 (K)	f
Laminar Flame Speeds	4	1	353	0.8-1.4
Ignition Delay Times	11	1-4	1000-2600	0.5-2

	No.	P_5 (atm)	T_5 (K)	f
OH, H_2O, CO_2, C_2H_4, CH_3 Species Profiles	11	1.6-2.4	1365-1545 K	1

Predictions of As-Compiled and Uncertainty-Minimized Models



Effect on Flame Speed Predictions

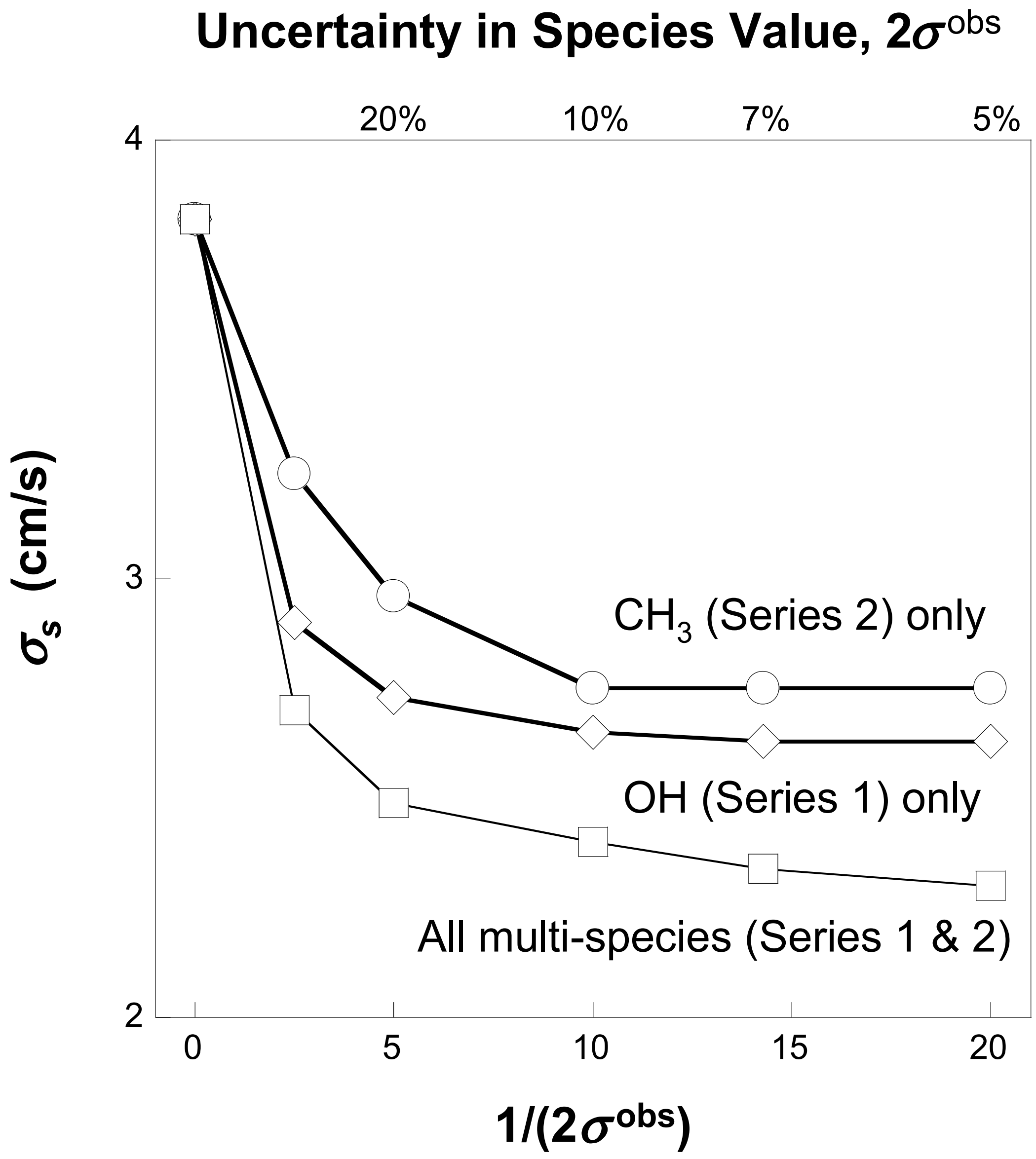


Considering no experiments

Model constrained by species profiles

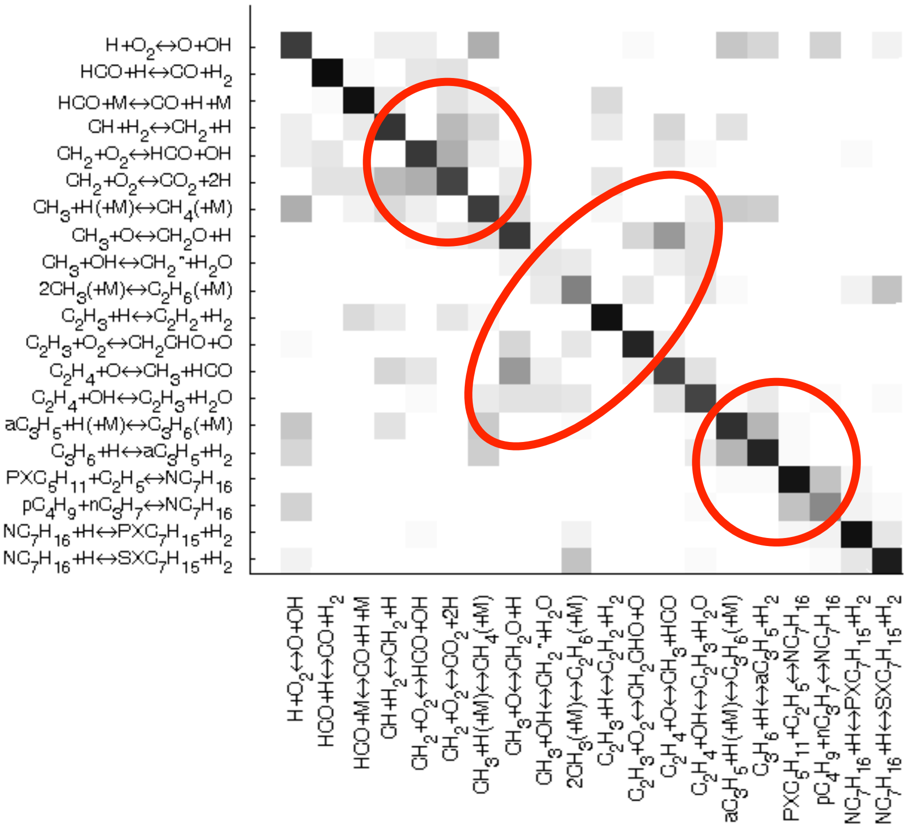
Model constrained by species profiles
+ flame speeds

Effect on Flame Speed Predictions

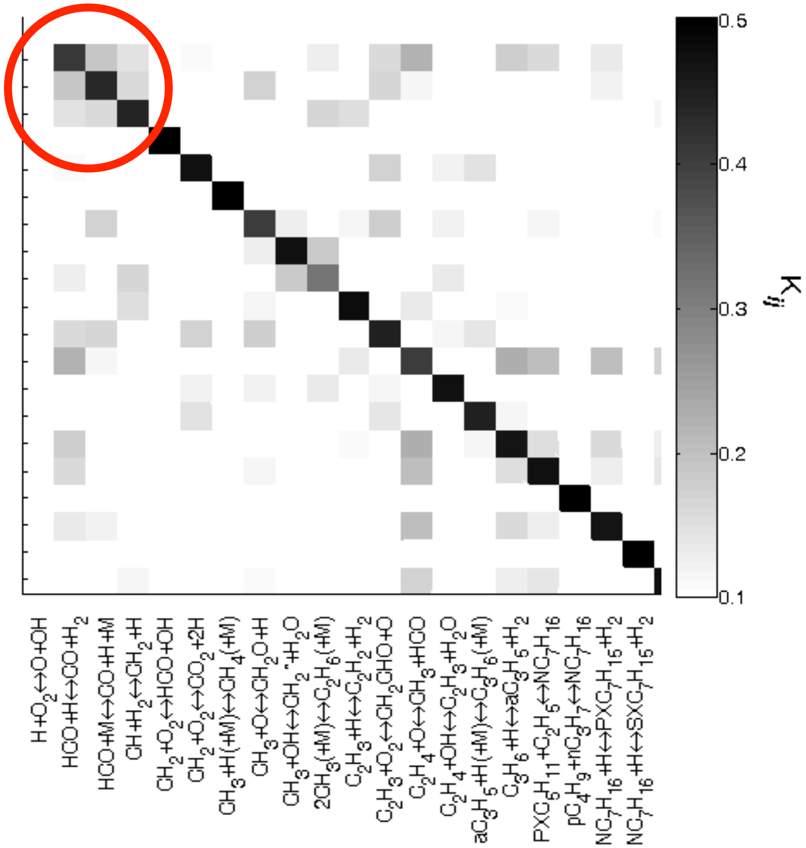


What did uncertainty minimization do?

Model constrained by species profiles



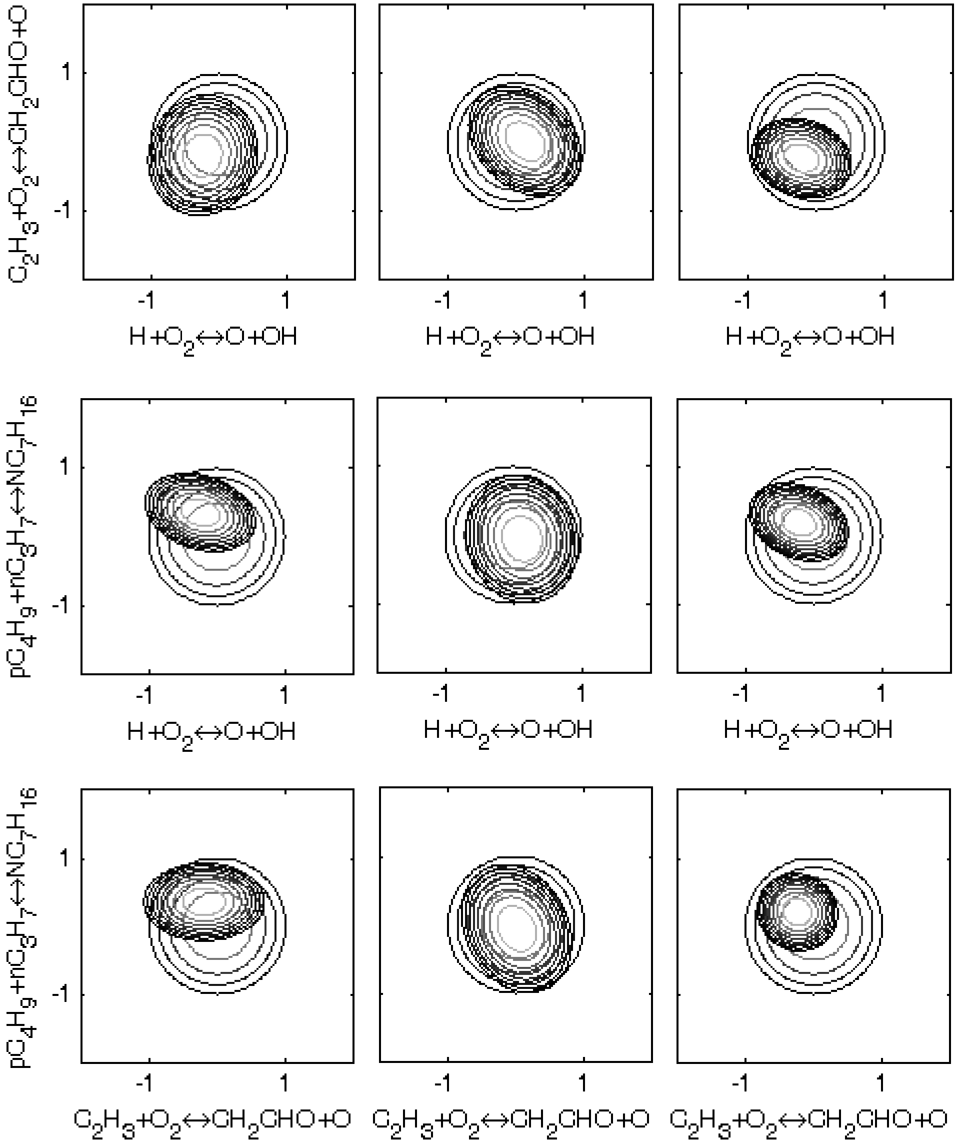
Model constrained by flame speeds



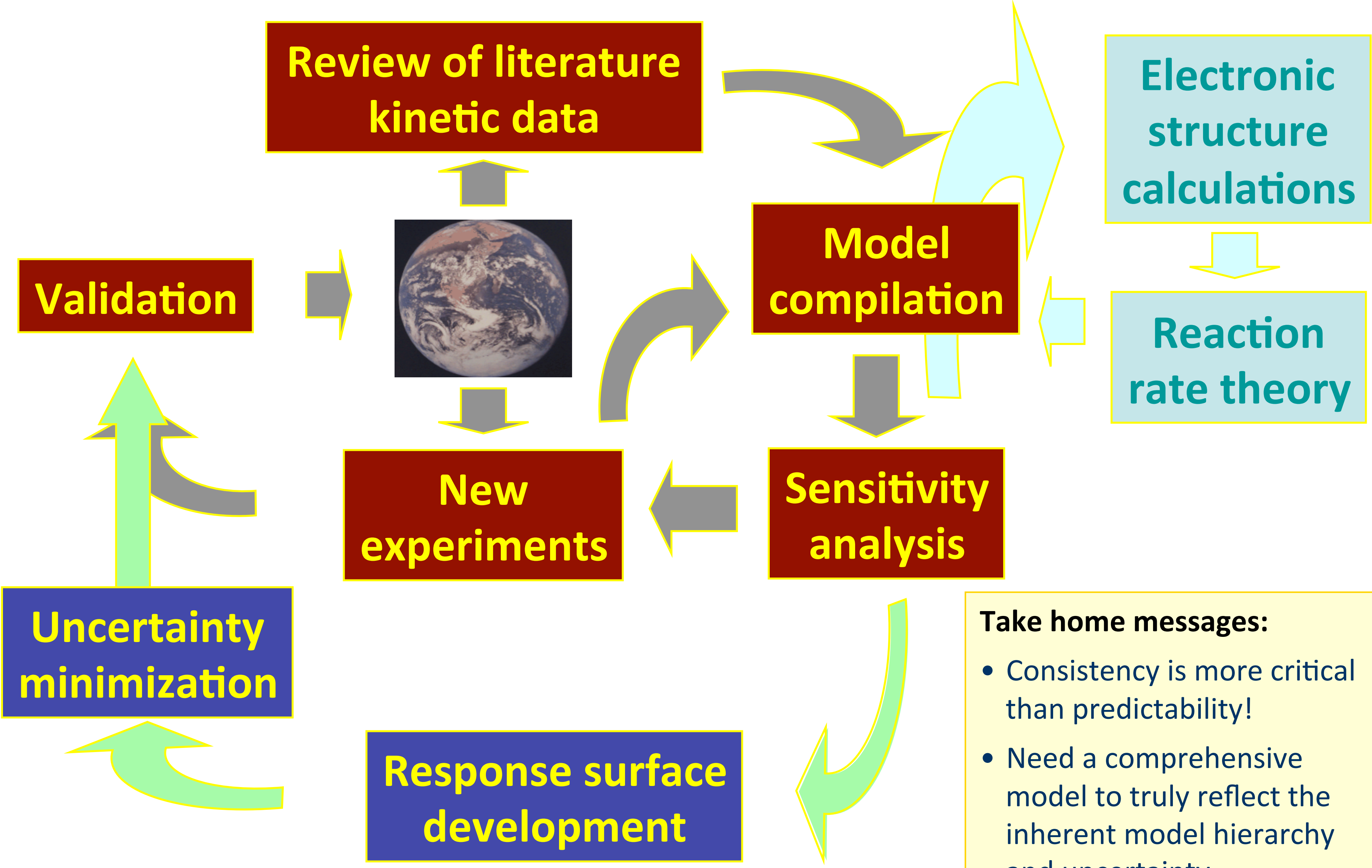
CH_3, CH_2, secondary chain branching, fuel breakup

H chain branching

What did uncertainty minimization do?



"Our" Approach



Review of literature kinetic data

Electronic structure calculations

Validation

Model compilation

Reaction rate theory

New experiments

Sensitivity analysis

Uncertainty minimization

Response surface development

Take home messages:

- Consistency is more critical than predictability!
- Need a comprehensive model to truly reflect the inherent model hierarchy and uncertainty.

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- Enoch Dames
- Bing yang

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- Chung-King Law (Princeton)
- Fokion Egolfopoulos (USC)
- Elke Goos (DLR)

The JetSurF team

Ron Hanson (Stanford)
Tom Bowman (Stanford)
Heinz Pitsch (Stanford)
Wing Tsang (NIST)
Angela Violi (UMich)
Peter Lindstedt (Imperial Col.)
Nick Cernansky (Drexel)
David Miller (Drexel)

Financial Support

AFOSR, AFRL, SERDP, DOE, NSF

Measurements of Elementary Rate Constants, Ignition Delays and Species Histories in Shock Tubes

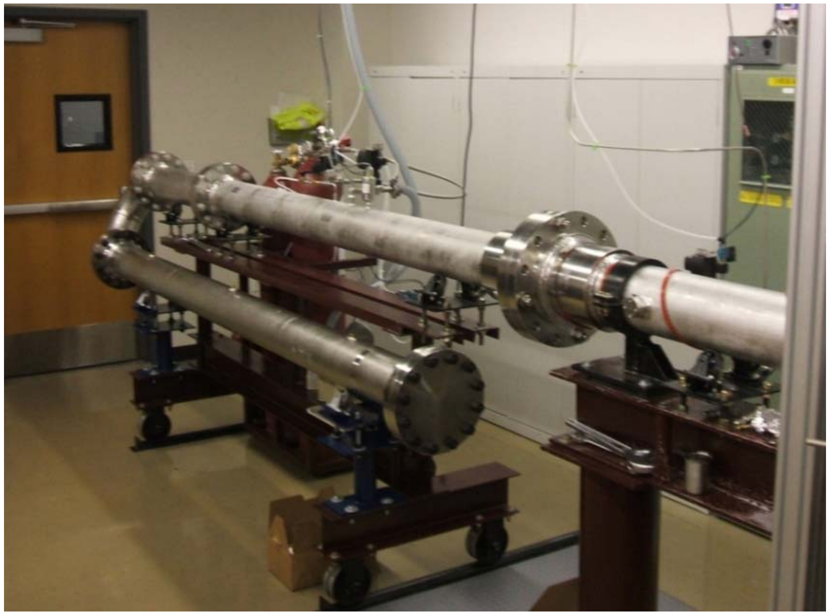
R. K. Hanson, D. F. Davidson

Stanford University

1st International Workshop on Flame Chemistry

July 28-29, 2012

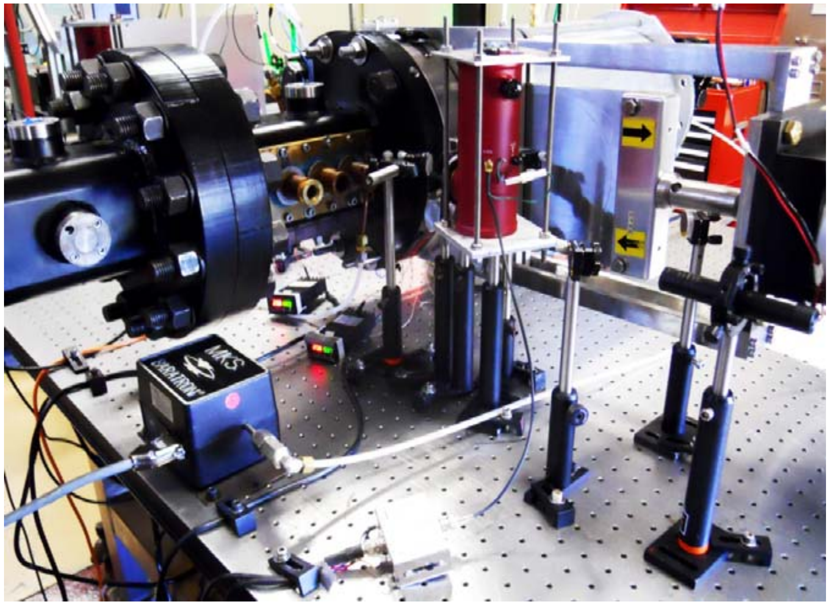
- Shock Tube/Laser Approach
- Advances in Methodology
- Elementary Reaction Rate Studies
- Multi-Species Time-Histories



Kinetics
Shock
Tube 1
(30 atm)

Kinetics
Shock
Tube 2
(30 atm)

Stanford Shock Tubes

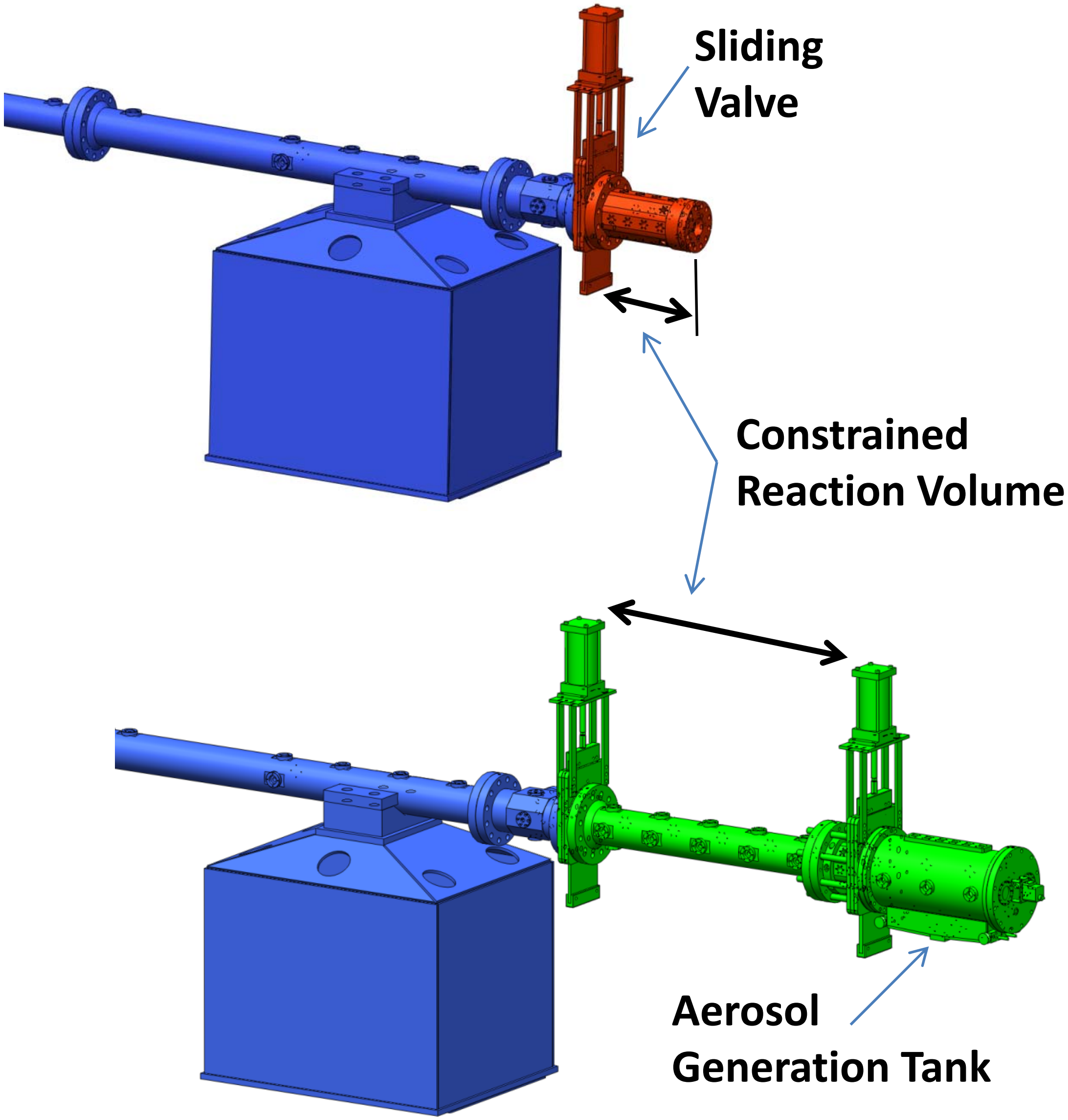


Aerosol
Shock
Tube
(10 atm)

High
Pressure
Shock
Tube
(500 atm)

New Constrained Reaction Volume (CRV) Facility

2 Configurations



Sliding Valve

Constrained Reaction Volume

Aerosol Generation Tank

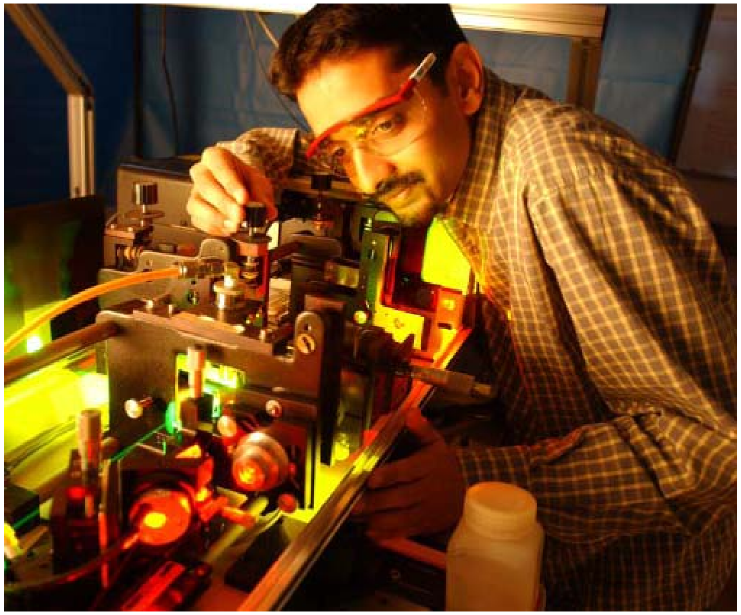
CRV-1

Gas-Phase Experiments to 100 atm

CRV-2

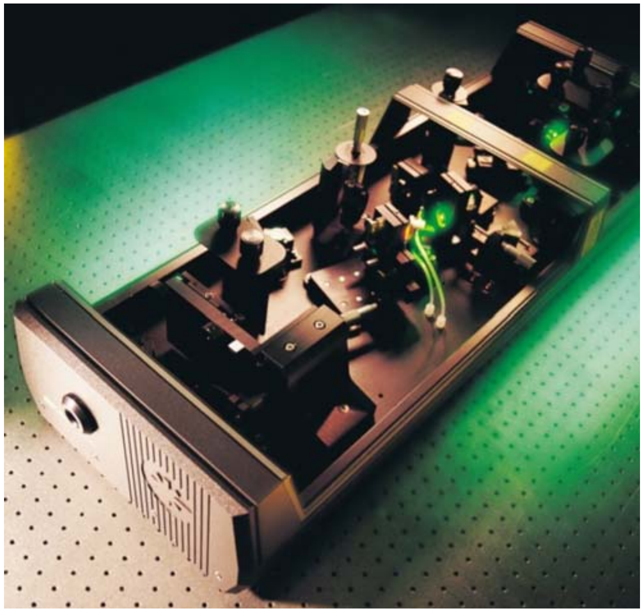
Aerosol Experiments to 100 atm

Stanford Laser Diagnostics



First use of tunable dye lasers in shock tubes (1982)

Ultra-fast lasers used to extend UV tuning range (2009)



Ultraviolet

CH_3	216 nm
NO	225 nm
O_2	227 nm
HO_2	230 nm
OH	306 nm
NH	336 nm

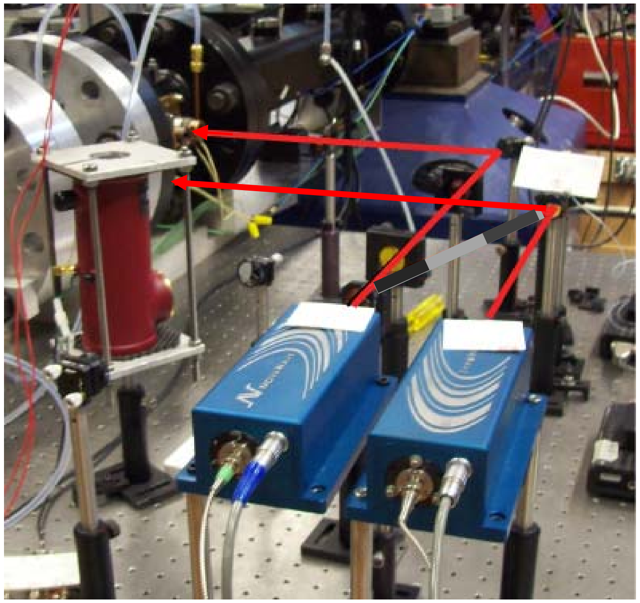
Visible

CN	388 nm
CH	431 nm
NCO	440 nm
NO_2	472 nm
NH_2	597 nm
HCO	614 nm

Infrared

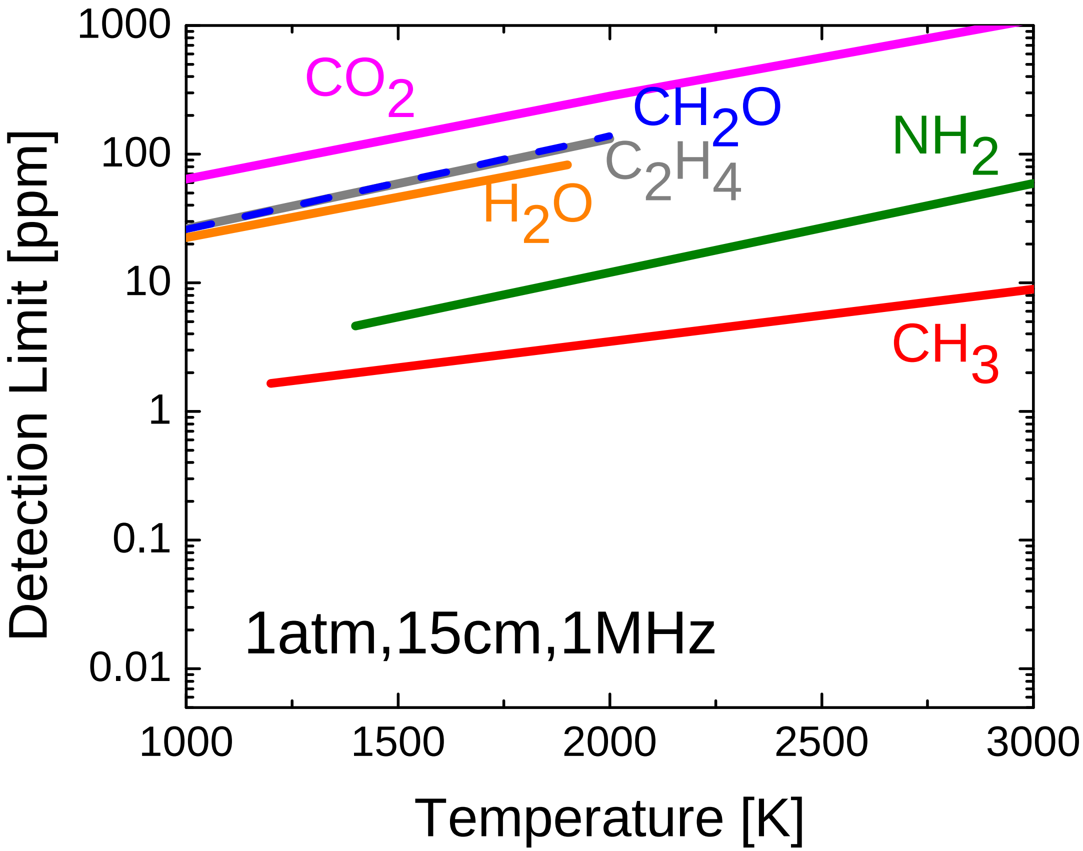
H_2O	2.5 μm
CO_2	2.7 μm
CH_4	3.4 μm
CH_2O	3.4 μm
CO	4.6 μm
NO	5.2 μm
C_2H_4	10.5 μm

New lasers allow simple access to mid-IR (2007-10)



Laser Absorption Yields High Sensitivity

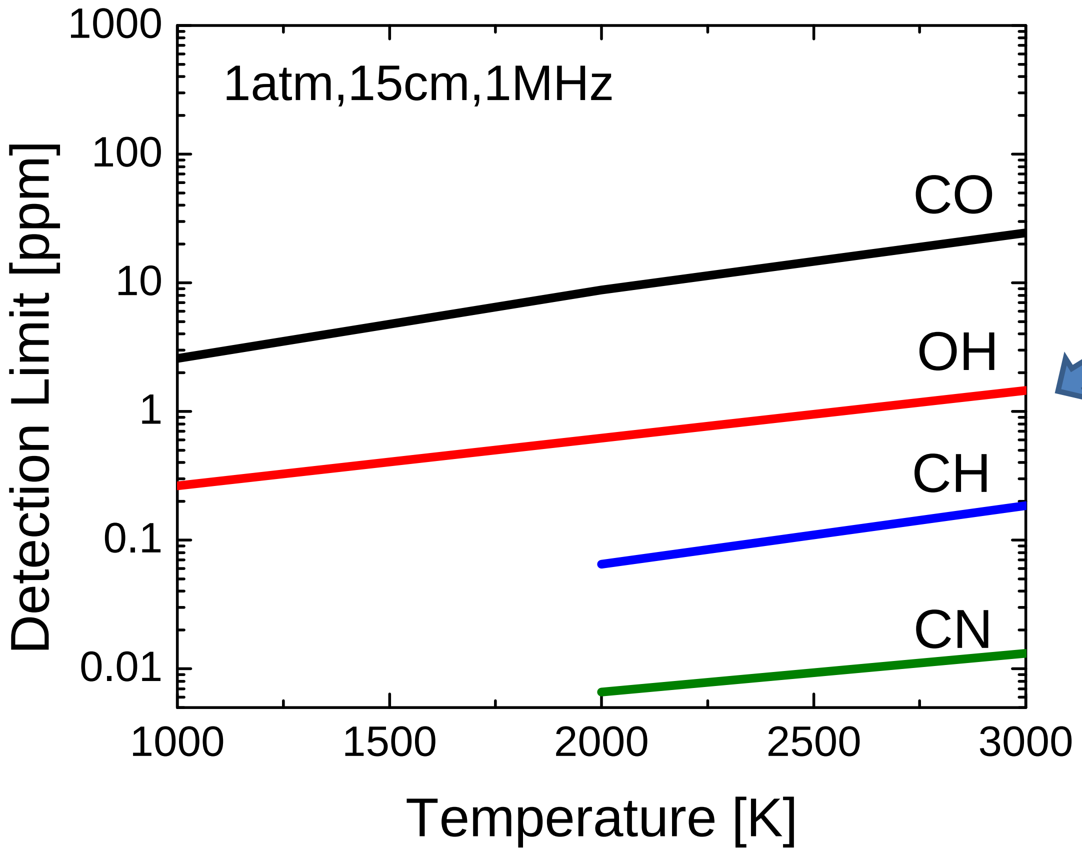
Representative Detection Limits: Polyatomic Molecules



- **Polyatomic molecules @ 1500K: 2-200 ppm**

Laser Absorption Yields High Sensitivity

Representative Detection Limits: Diatomic Molecules

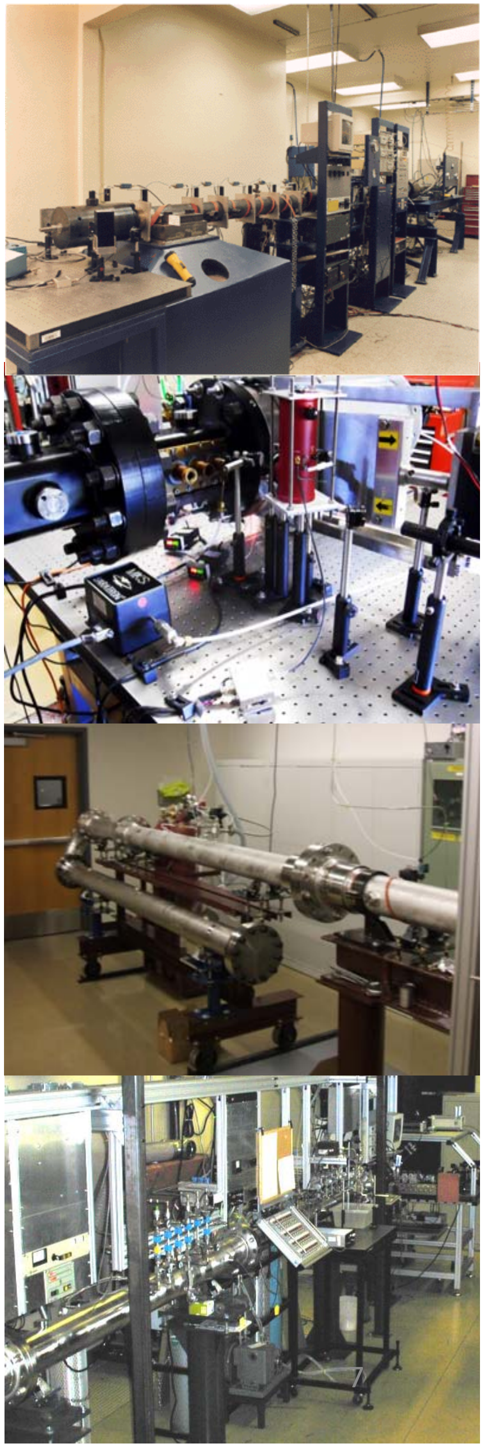


sub-ppm sensitivity for OH, CH, CN

- **Diatomic molecules @ 1500K:**
  - **- sub-ppm detectivitiy for UV absorbers**
  - **- ppm detectivity for IR absorbers**

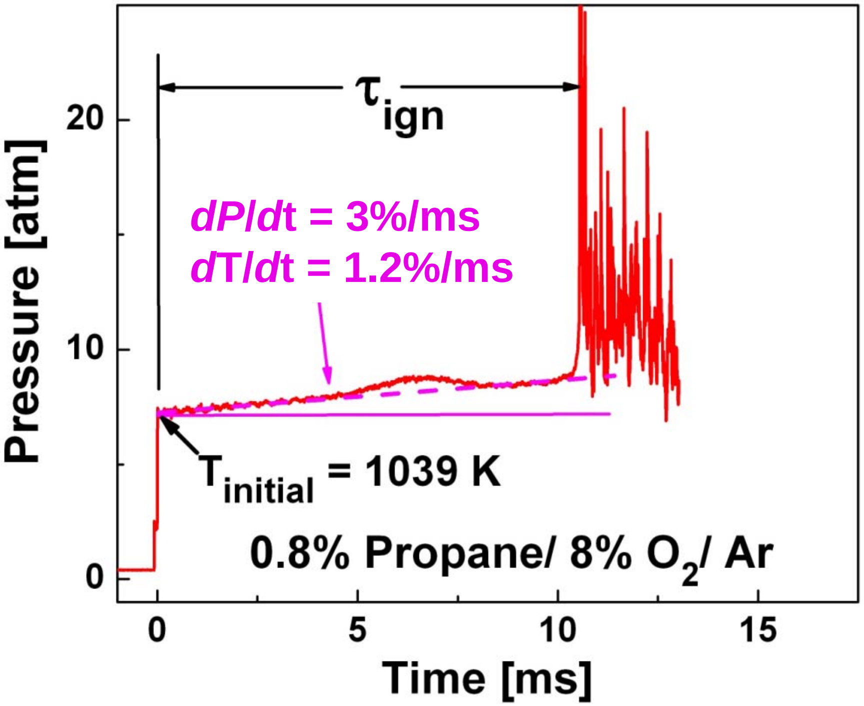
Advances in Shock Tube Methodology

1. **Improved uniformity with driver inserts**
2. **Longer test times with tailored gas mixtures & extended driver**
3. **Reactive gas modeling: problem and solutions**



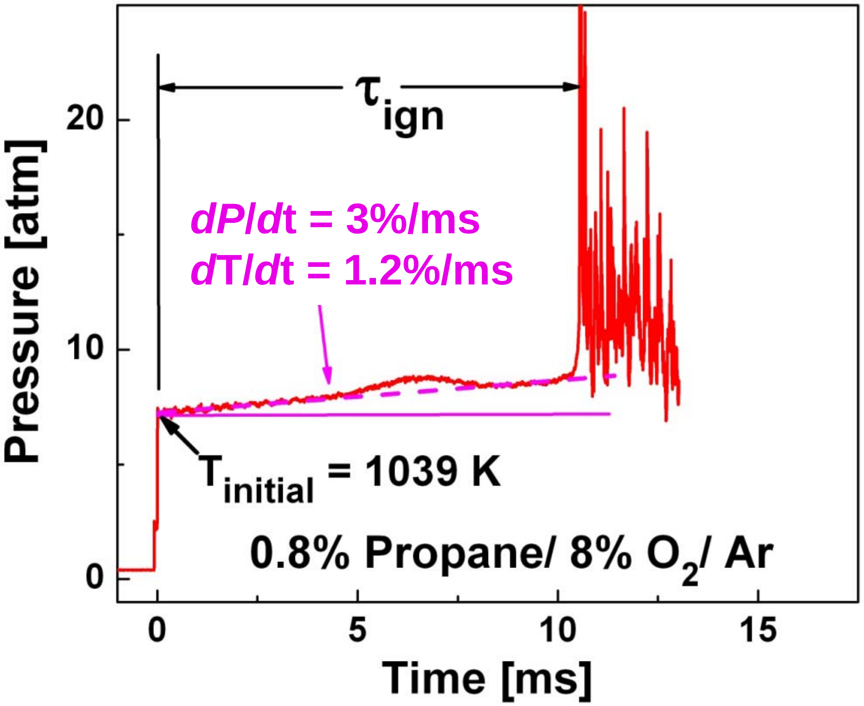
Improvement in Reflected Shock Temperature Uniformity Using Driver Inserts

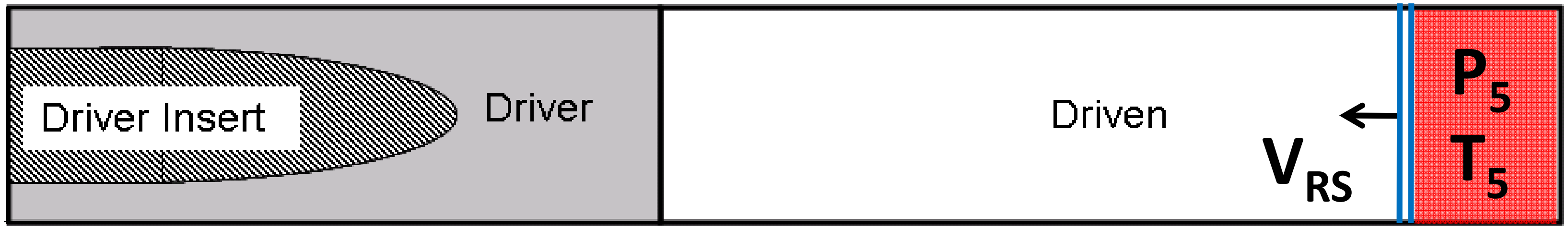
- **Conventional shock tube operation can provide near-ideal uniform flows for 1-3 ms**
- **But, boundary-layers and attenuation induce dP/dt and dT/dt at longer times**



Improvement in Reflected Shock Temperature Uniformity Using Driver Inserts

- **These effects reduce ignition delay times relative to Constant P case**
- **Solution: Driver Inserts**



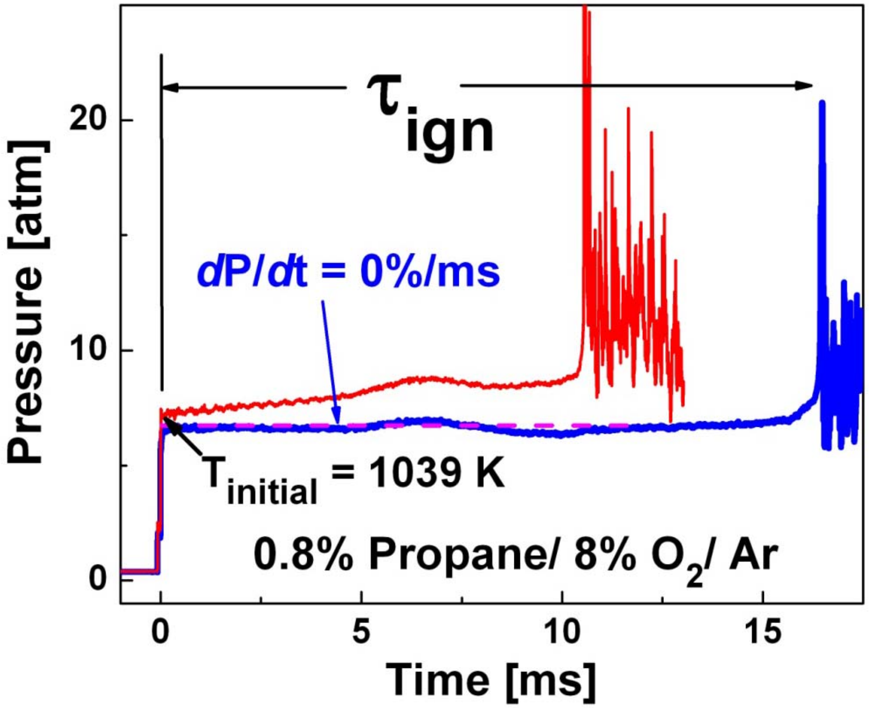

Driver Insert
Driver
Driven
V RS
P 5
T 5

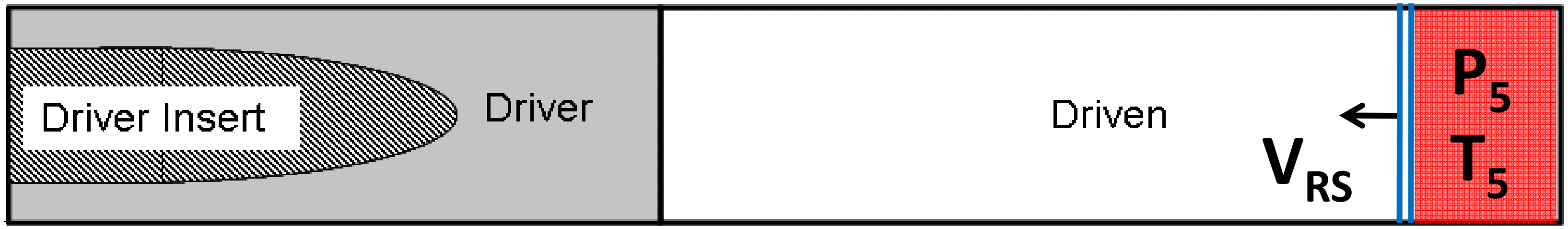
- **Driver inserts modify flow to achieve uniform T and P at long test times**

Improvement in Reflected Shock Temperature Uniformity Using Driver Inserts

- **Result: dP/dt = 0 prior to ignition**

→ Proper τ_{ign} for comparison with Constant P simulations

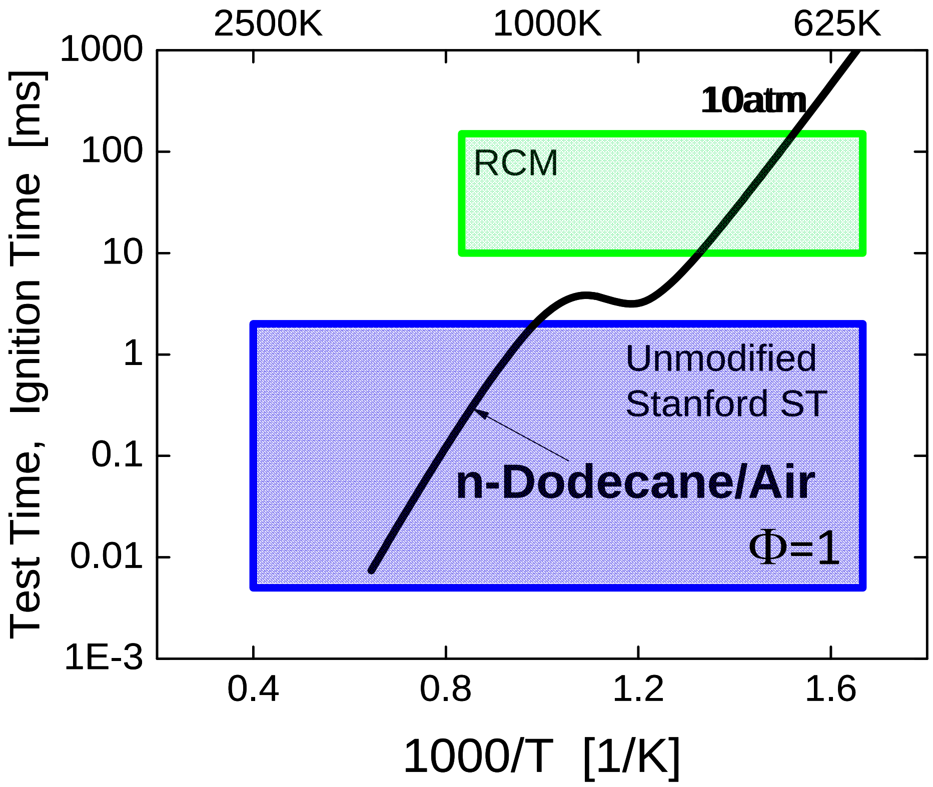




Driver Insert
Driver
Driven
V_{RS}
P_5
T_5

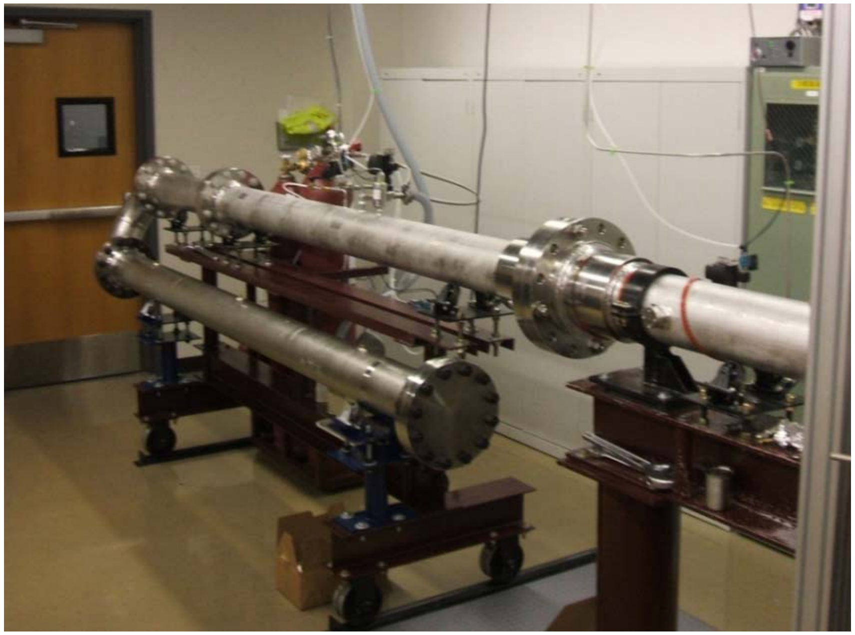
Longer Test Times Achievable with Tailored Gas Mixtures & Extended Driver Sections

- **Conventional shock tube operation: ~ 1-3 ms test time**
- **No overlap with RCM operation~ 10-150 ms test time**

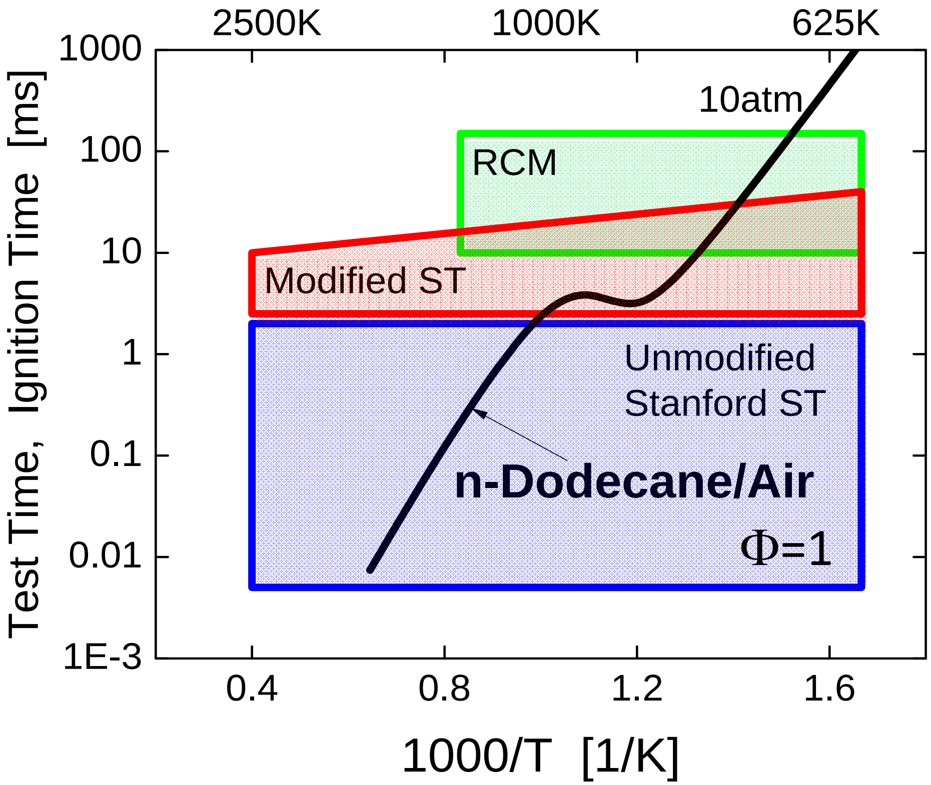


Longer Test Times Achievable with Tailored Gas Mixtures & Extended Driver Sections

- **Longer driver length and tailored gas mixtures can provide longer test times (> 40 ms)**



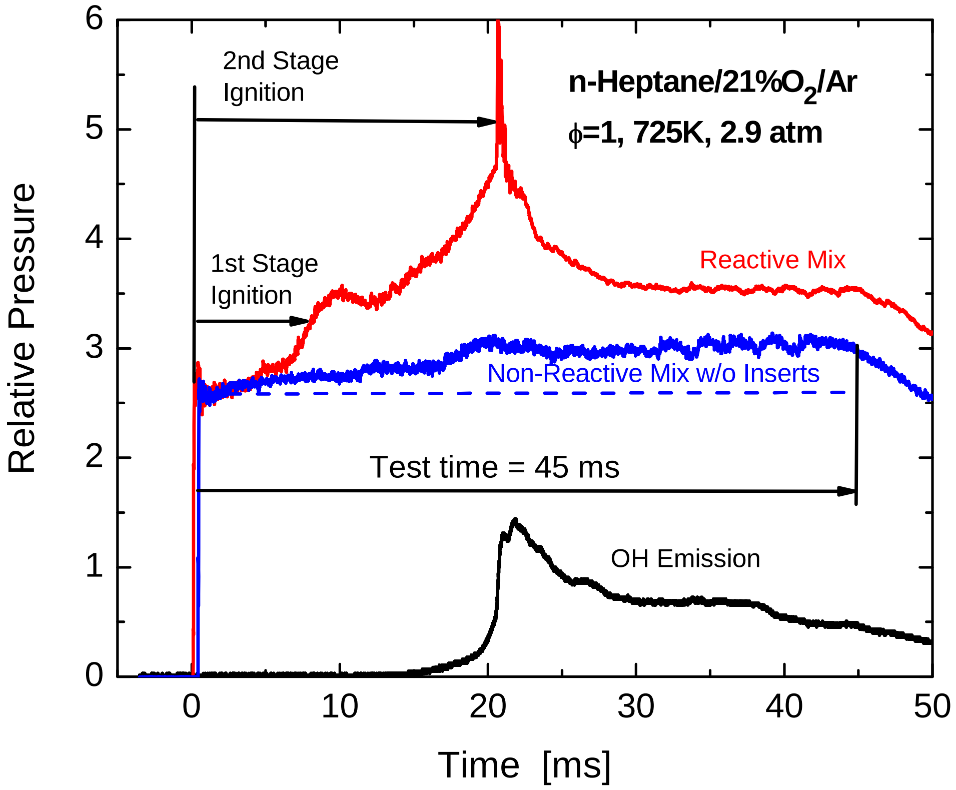
2x Driver Extension



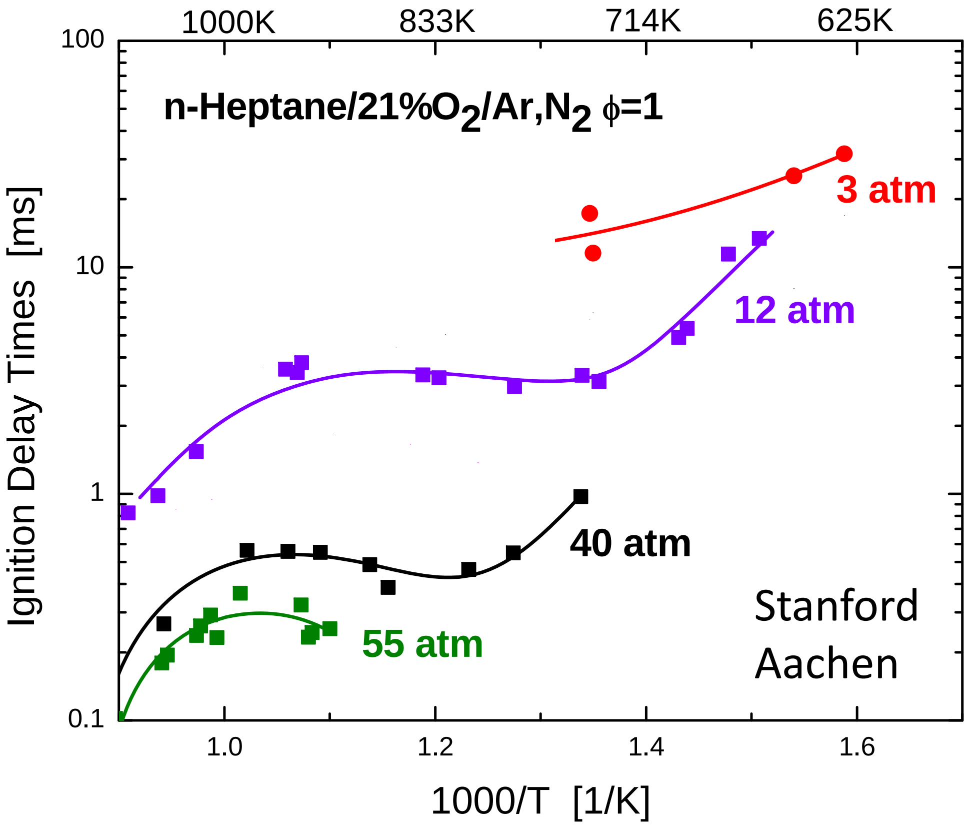
- **Shock tubes now can overlap with RCMs**

First Use of Long Test-Time Facility: Low Pressure n-Heptane Ignition in the NTC regime

- **Test time = 45 ms at 725K**
- **Enables first low-pressure (~3 atm) n-heptane ignition data in NTC regime**
- **Clear evidence of 2-stage ignition: τ_1 = 8 ms, τ_2 = 20 ms**
- **Next step: add driver inserts to remove *d*P/*d*t & *d*T/*d*t**
- **How do the 3 atm data compare to high P data?**

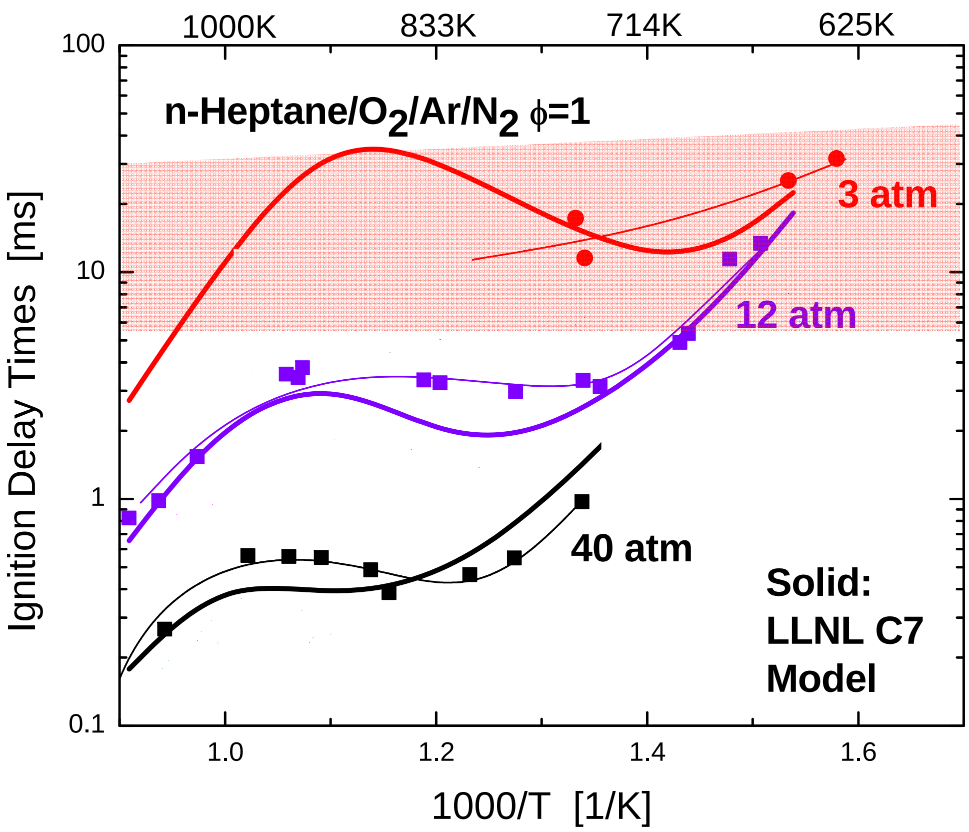


Low-Pressure, Low-Temperature Studies: New Results for n-Heptane in the NTC Regime



- **Previous 12-55 atm data**
- **New 3 atm data**
- **How do measurements compare with current models?**

Low-Pressure, Low-Temperature Studies: NTC Heptane, Comparison with Model



- LLNL C7 (2000) model performs reasonably well at high P
- Further tests needed at low P
- Reveals value of long test time experiments

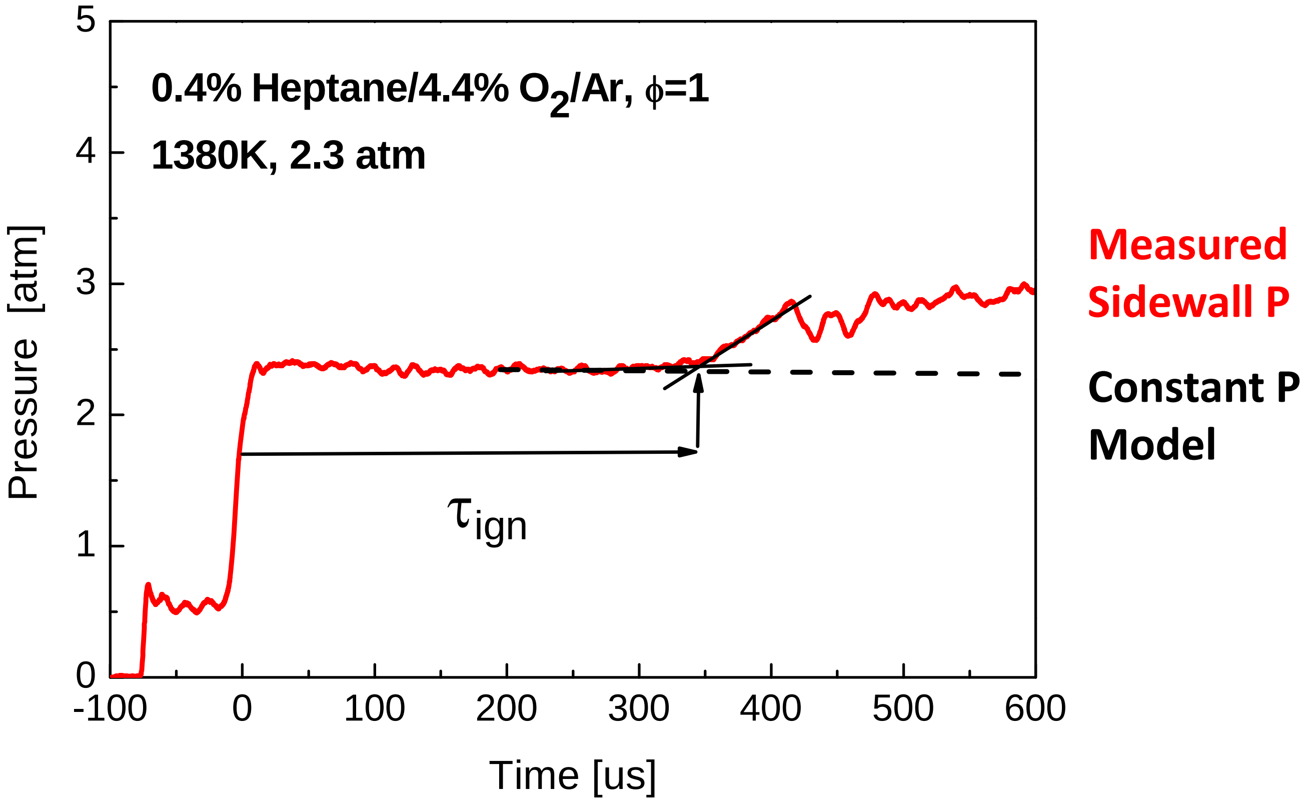
Reactive Gasdynamics Modeling: A Problem

- **Most current reflected shock modeling assumes Constant-Volume or Constant-Pressure**

But:

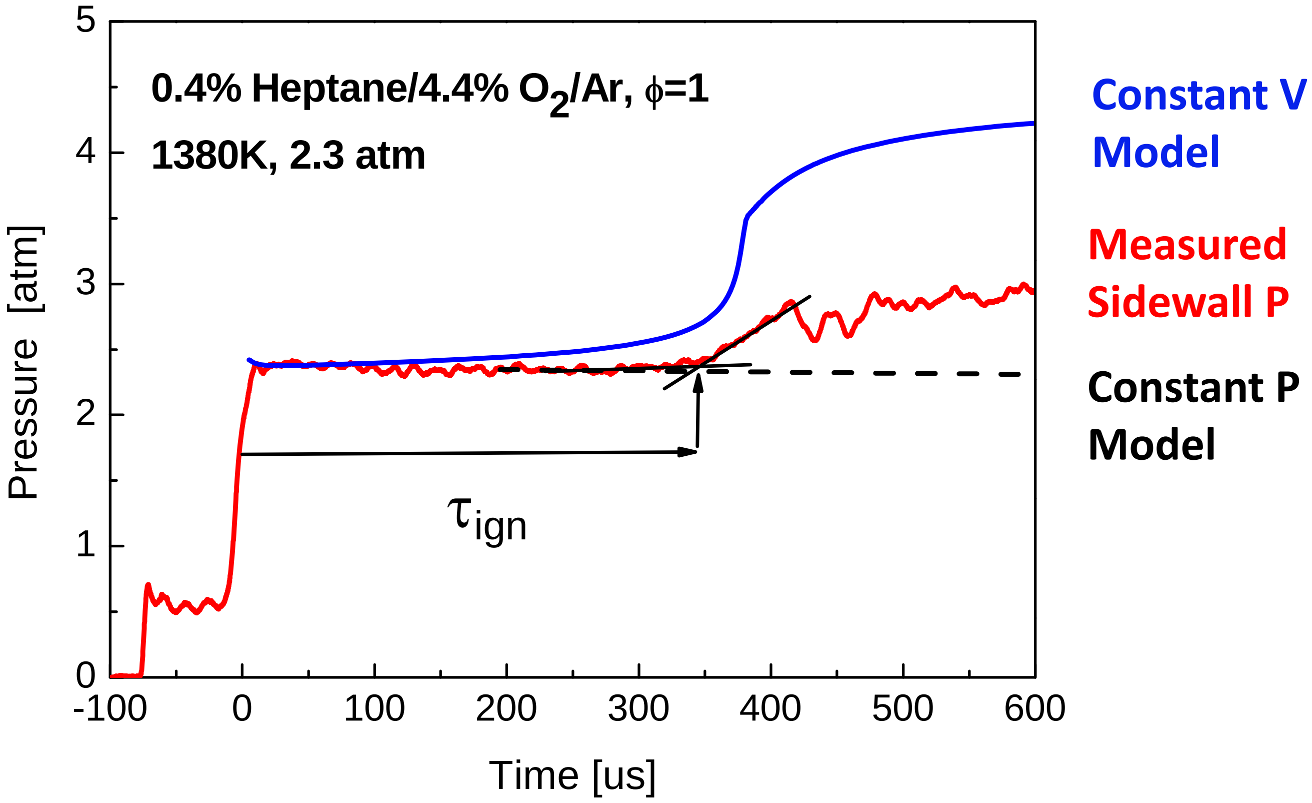
- **Exothermic energy release during oxidation or endothermic cooling during pyrolysis changes T & P behind reflected shocks**
  → not a Constant-V or Constant-P process!
- **Example: Heptane Ignition**

Effect of Energy Release on P Profiles: n-Heptane Oxidation



- **How does this compare with models?**
- **Not a constant P process!**

Effect of Energy Release on P Profiles: n-Heptane Oxidation



- **How does this compare with model?**
- **Not a constant P process!**
- **Not a Constant-V process, even for 0.4% fuel!**
- **So how can entire process be modeled?**

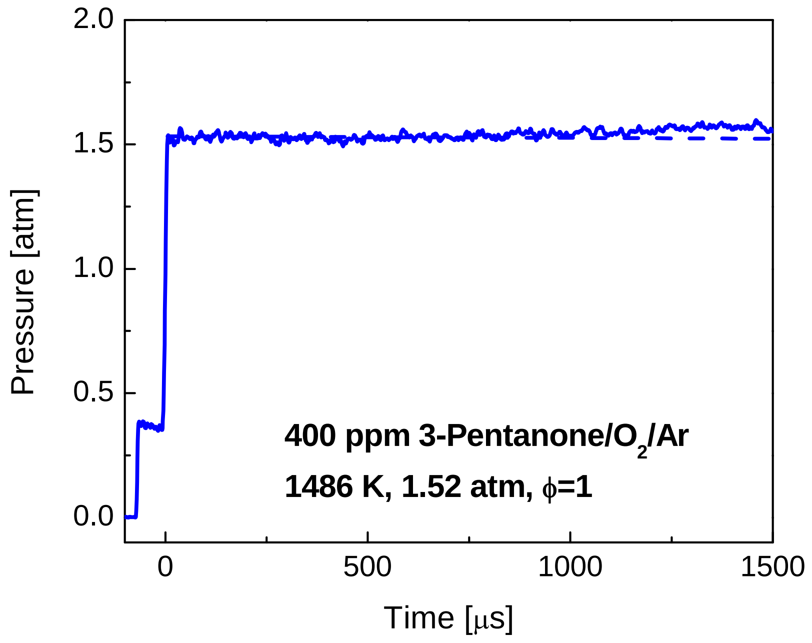
3 Proposed Solutions to Enable Modeling through Entire Combustion Event

1. **Minimize fuel loading to reduce exothermically- or endothermically-driven T and P changes**
   - enabled by high-sensitivity laser diagnostics
2. **Modified gasdynamics modeling to account for P and T change during combustion**
   - work in progress (but computationally intensive: 1-D, 3-D)
3. **Use new constrained reaction volume concept to minimize pressure perturbations**
   - enables constant P (or specified P) modeling

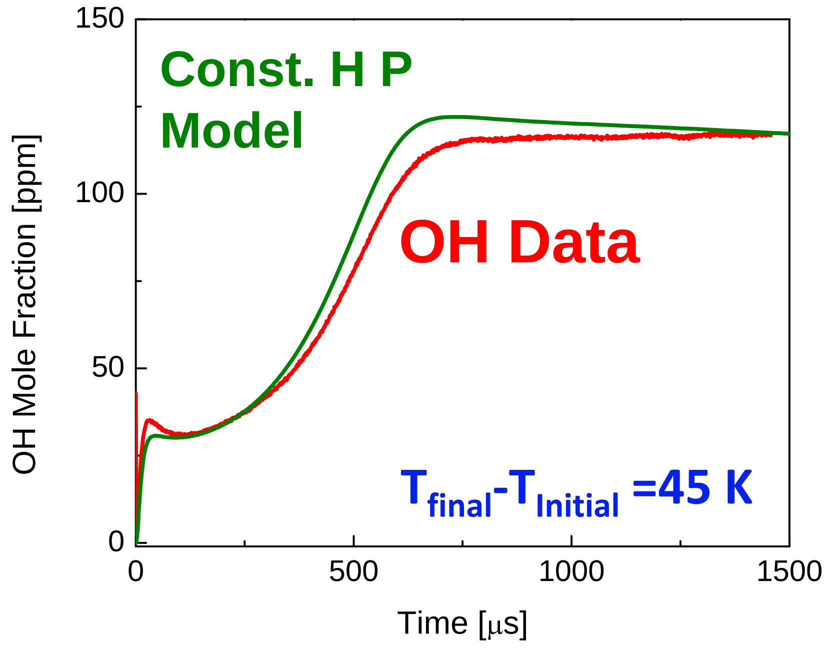
Examples: **1) Use of dilute reactive mixtures**
2) Use of constrained reaction volume

Example 1: Benefit of Dilute Mixtures
3-Pentanone Oxidation

Low Fuel Loading Experiment



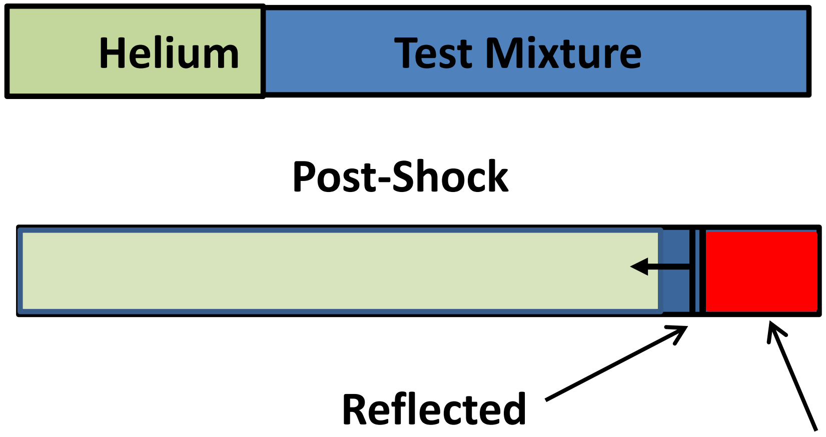
OH Mole Fraction



- **Pressure nearly constant throughout experiment**
- **Good agreement between Constant H,P model and expt.**
- **Model successfully includes temperature change**

Example 2: Constrained Reaction Volume Approach
Hydrogen Ignition at 950 K

Conventional Shock Tube



Pre-Shock

Helium

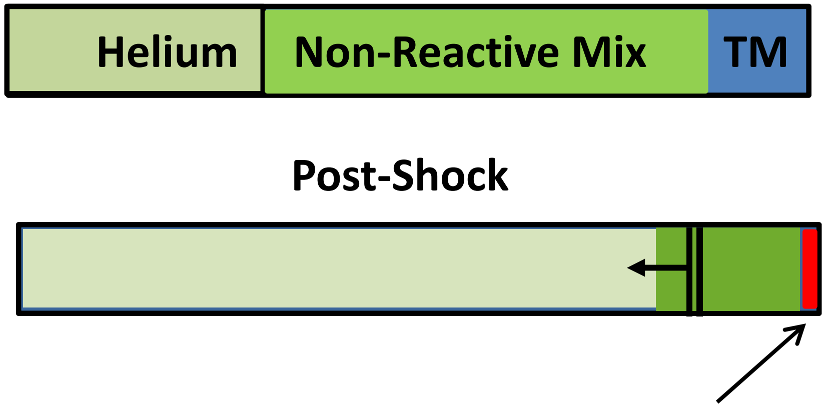
Test Mixture

Post-Shock

Reflected Shock Wave

Large Region of Energy Release

Constrained Reaction Volume



Pre-Shock

Helium

Non-Reactive Mix

TM

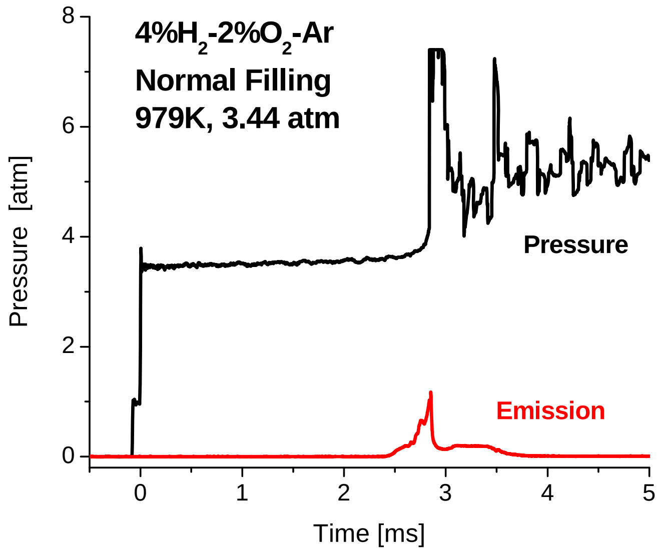
Post-Shock

Small Region of Energy Release

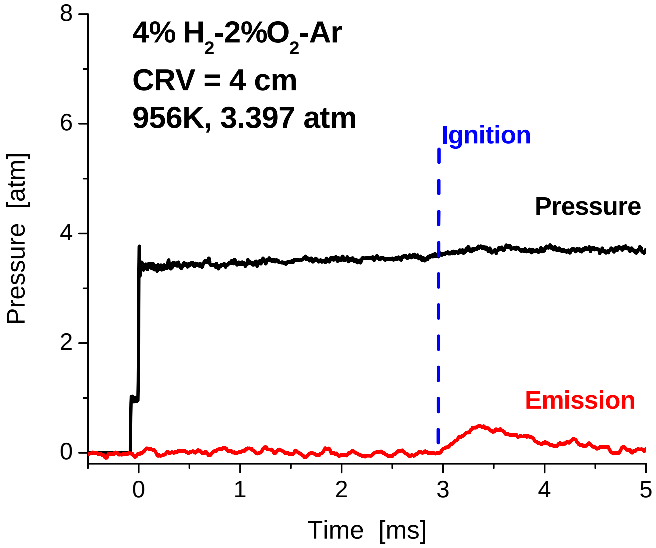
- **Large reaction volume gives large energy release → ΔP & ΔT**
- **CRV gives reduced energy release → near-constant P**

Example 2: Constrained Reaction Volume Approach Hydrogen Ignition at 950 K

Conventional Shock Tube



Constrained Reaction Volume



- **Conventional ST exhibits large pressure change!**
- **CRV pressure nearly constant throughout experiment!**
- **Allows kinetics modeling through ignition and combustion!**

Elementary Reaction Rate Determinations

Goal

Near-direct determination of rate constants for specific reactions

Examples

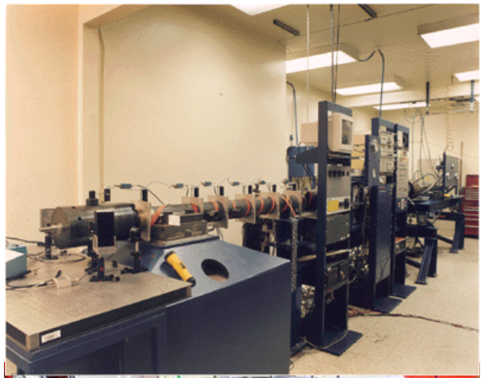
OH + ketones:

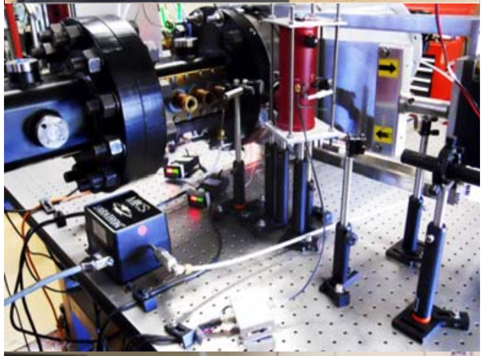
acetone, 2-butanone, 2- & 3-pentanone

OH + alkanes

OH + butanol isomers

OH + methyl esters

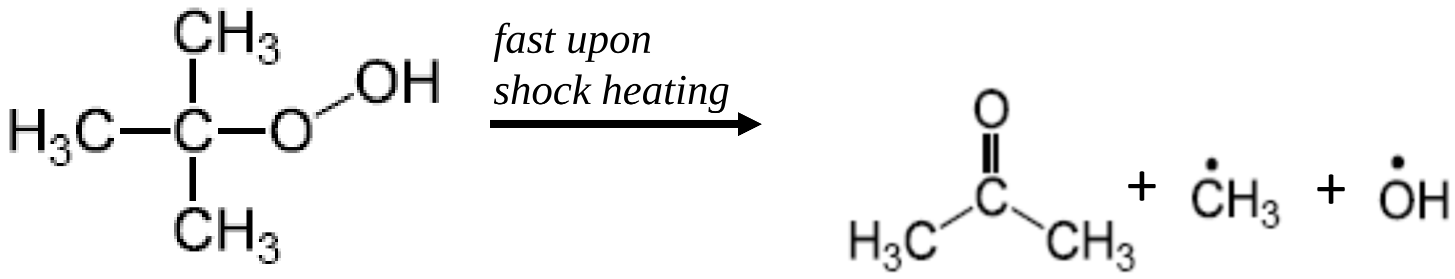




Experimental Strategy

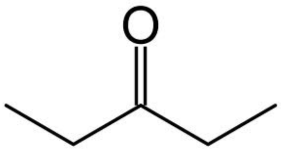
- TBHP used as a prompt OH precursor
  - Useful T range (850 to 1350 K)
  - Pioneered by Bott and Cohen (1984)
  - Also used at Argonne

- Fuel in excess, pseudo-first order experiment

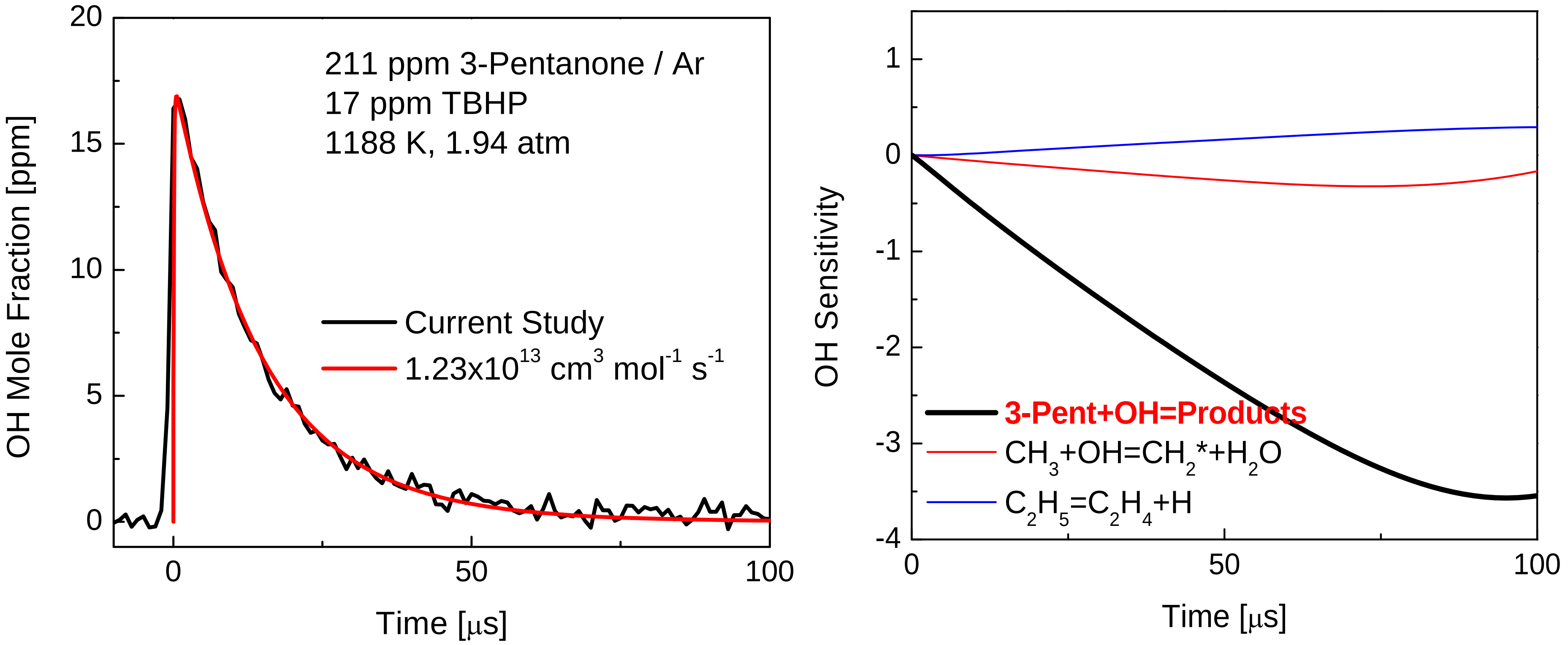


tert-butylhydroperoxide

Acetone

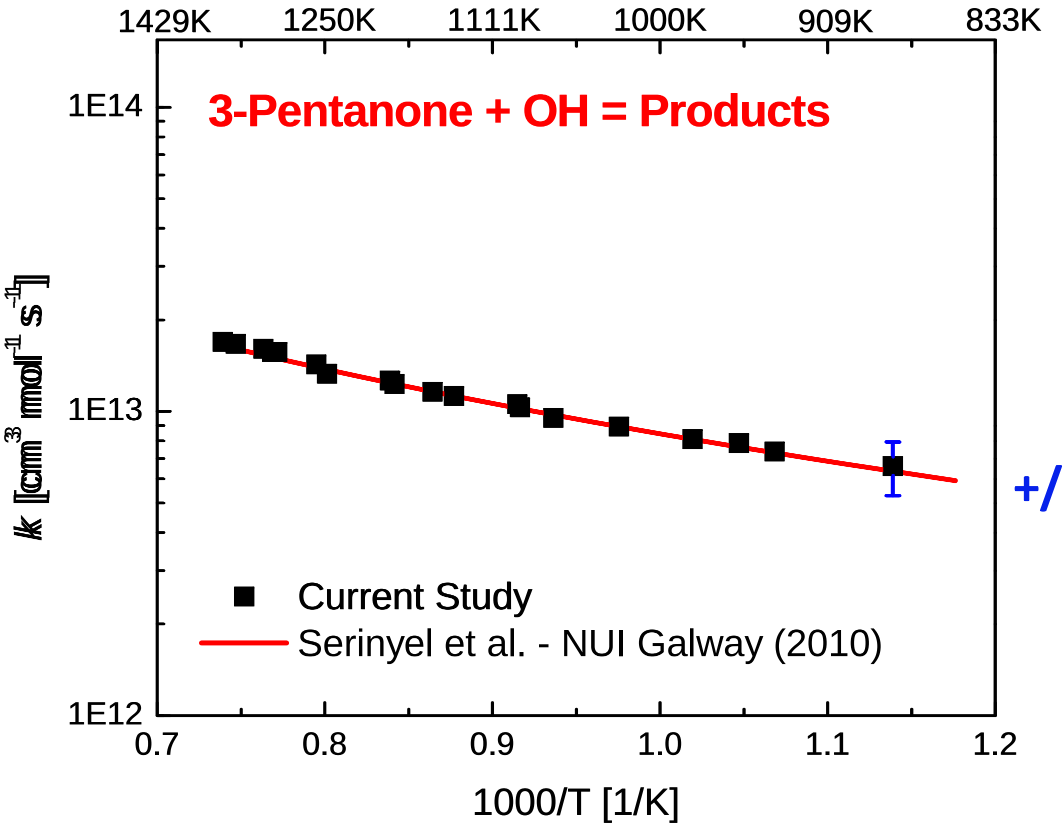


Representative 3-Pentanone+OH Data: 1188 K and 1.94 atm



- **High-quality data allows high-precision comparison with model**
- **Sensitivity analysis confirms pseudo-first order behavior**
- **Near-direct determination of reaction rate constant!**

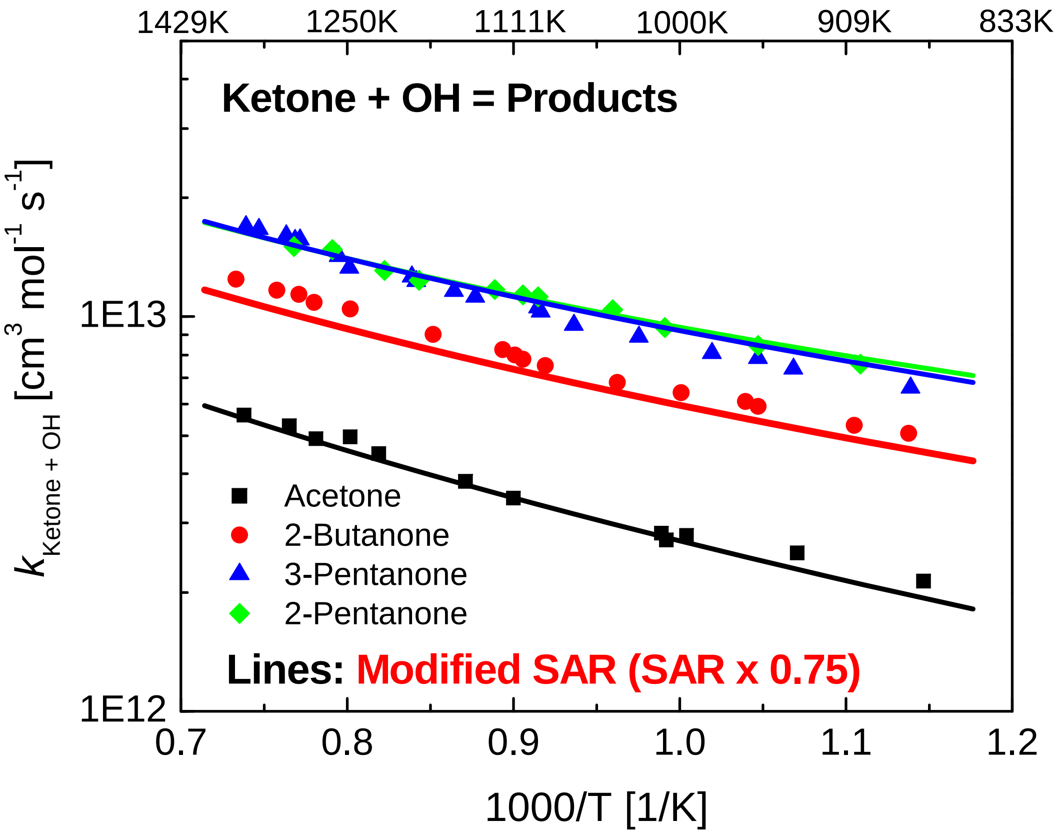
Results for 3-Pentanone + OH → Products



+/- 20%

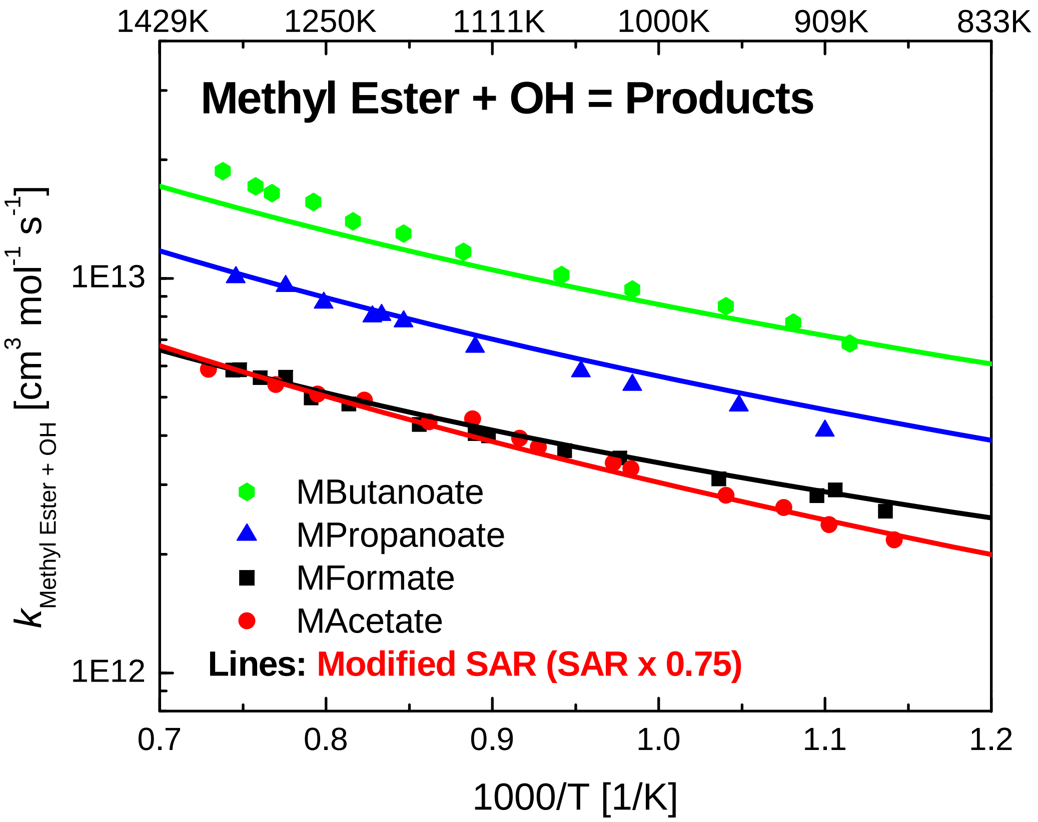
- **No other high temperature data available**
- **NUI model (Serinyel et al.) in excellent agreement**

Summary: OH+Ketones→Products



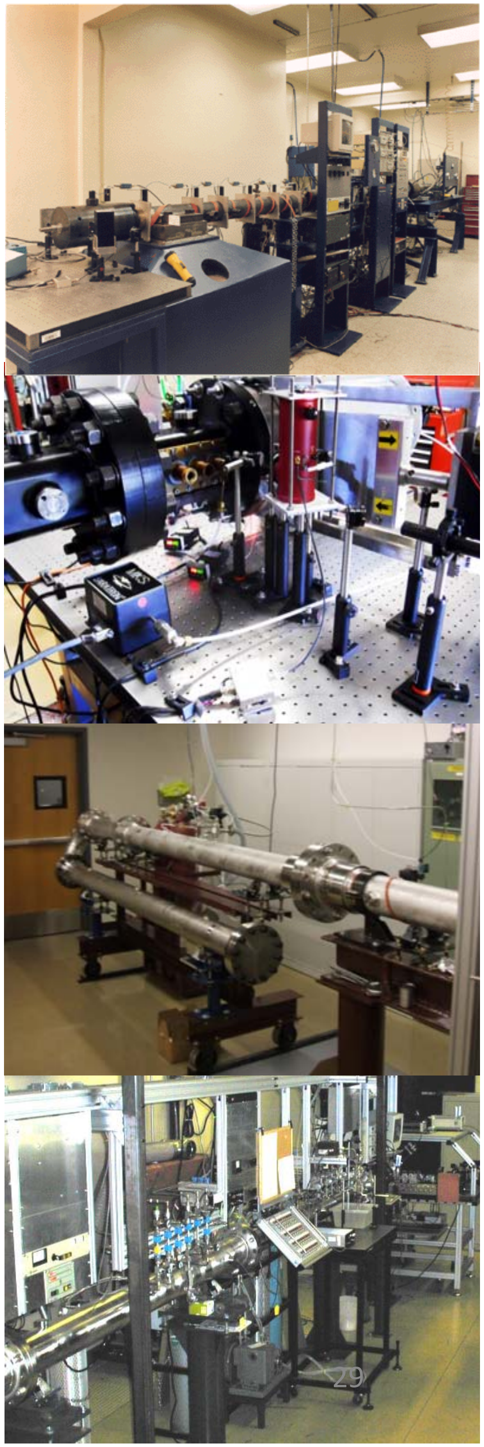
- **How do data compare with Structural Activity Relationship (SAR) model?**
- **Data agree within 25% with SAR-estimated rate constants**
- **Similar measurements performed with methyl esters**

Summary: OH+Methyl Esters → Products



- **Data agree within 25% with SAR-estimated rate constants**
- **Current work: OH + aldehydes, alcohols**

Multi-Species Time-Histories



Motivation

Multi-species provide greater constraint on mechanism refinement/evaluation

Recent Work

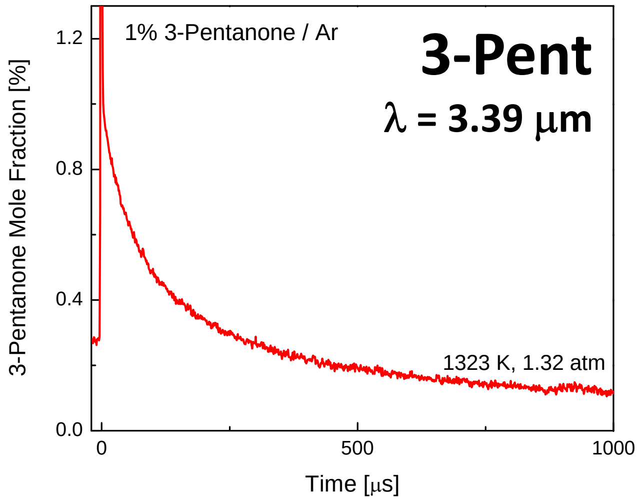
Ketones: Acetone, Butanone, 3-Pentanone

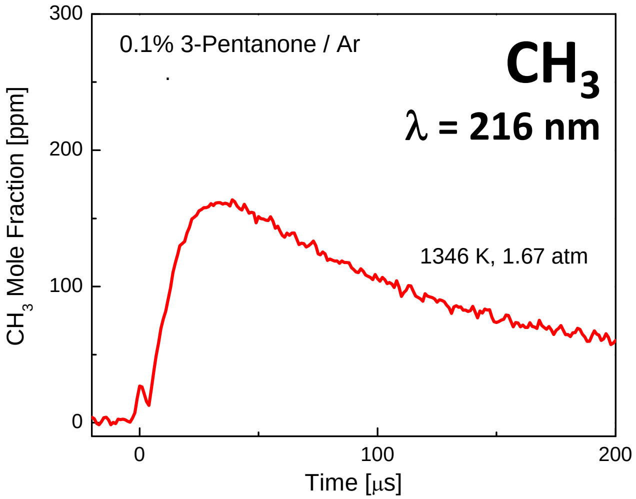
Alcohols: 1-, 2-, tert-,& iso-Butanol

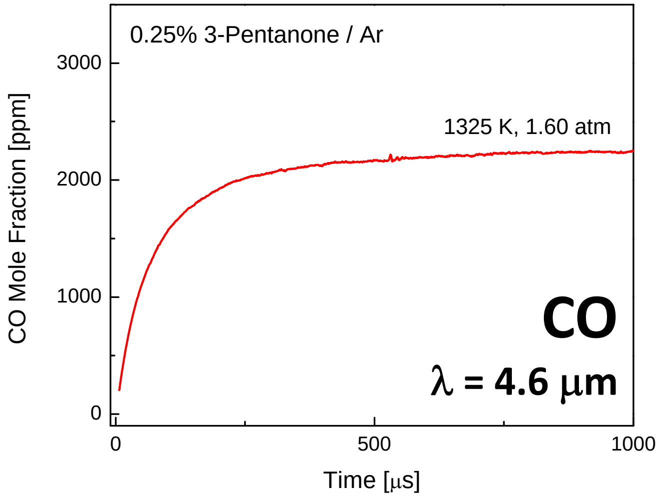
Alkanes: n-Hexadecane

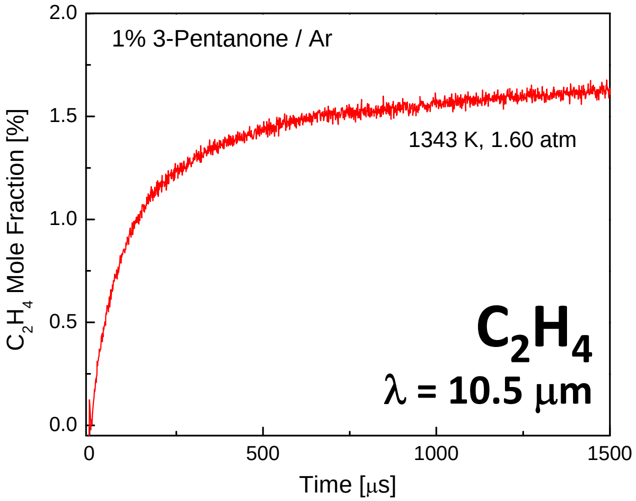
Esters: Methyl Formate, MA, MP, MB, EP

Multi-Species Approach: 3-Pentanone Pyrolysis



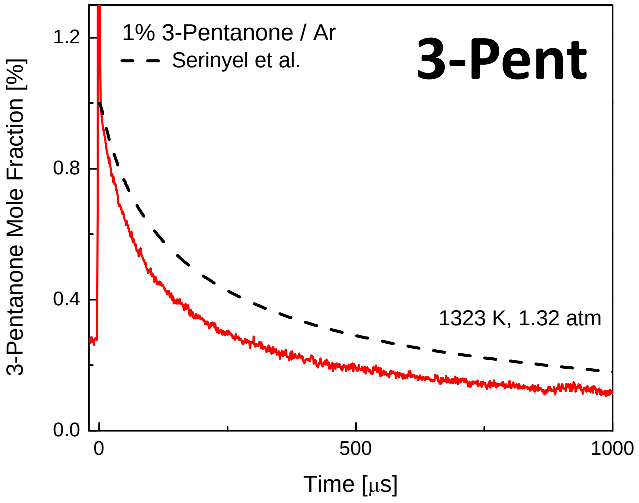


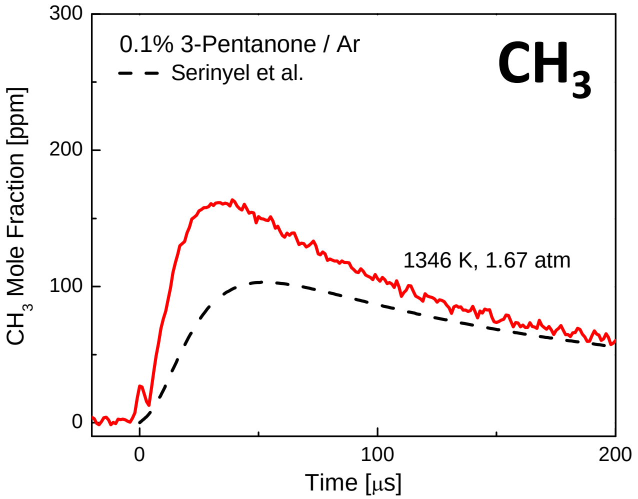


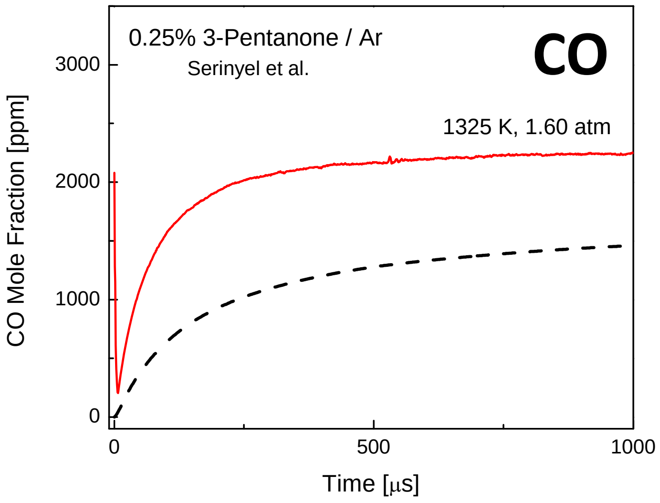


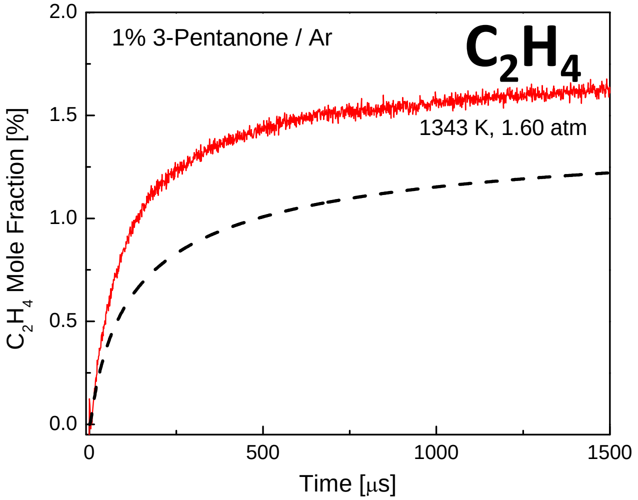
Excellent SNR, high sensitivity data

Comparison with Serinyel et al. (2010) Galway NUI





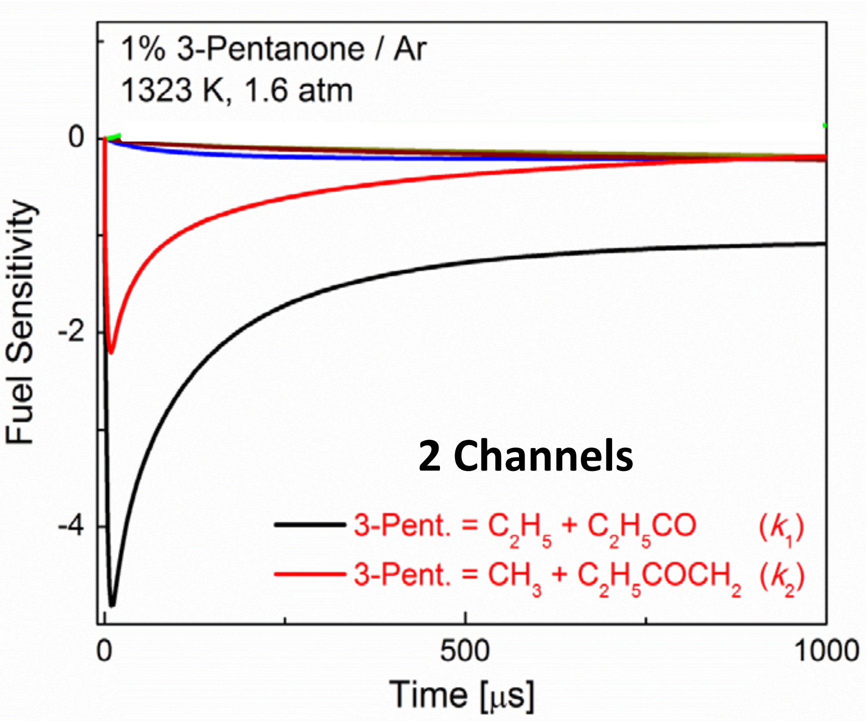




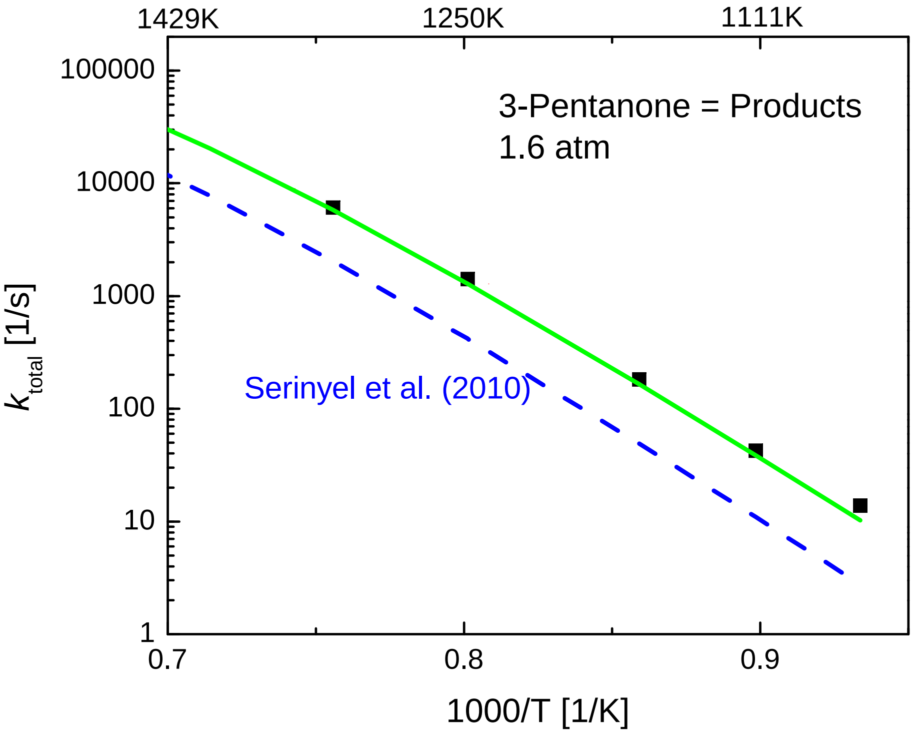
Two Differences: 1) 3-P decomposition rate; 2) CO/C_2H_4 yields

3-P Data Enables Revision of Decomposition Rate

3-Pentanone Sensitivity



Arrhenius Plot: 3-Pent → Products

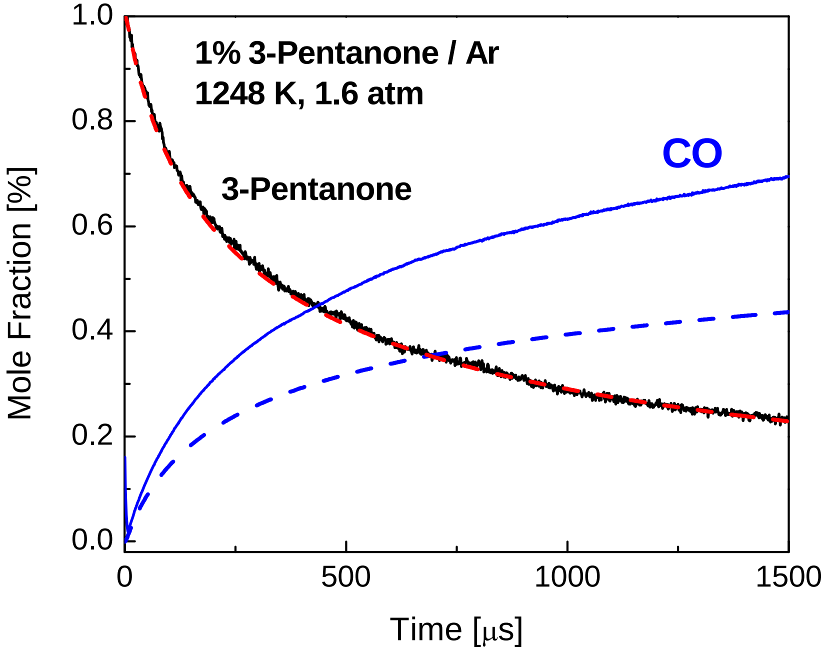


- 3-P data show strong sensitivities to $k_1 + k_2$

- Revised k_{total} 3.5x Serinyel et al. rate
- CO yields still not correct!

CO Yield Resolved through Use of O-Atom Balance

3-P and CO data yield total O-atoms



O-atom concentration at 1.5 ms

Laser Absorption

3-Pentanone:	**23%**
CO:	**69%**
Sum:	**92%**

Simulation (with new k_1+k_2)

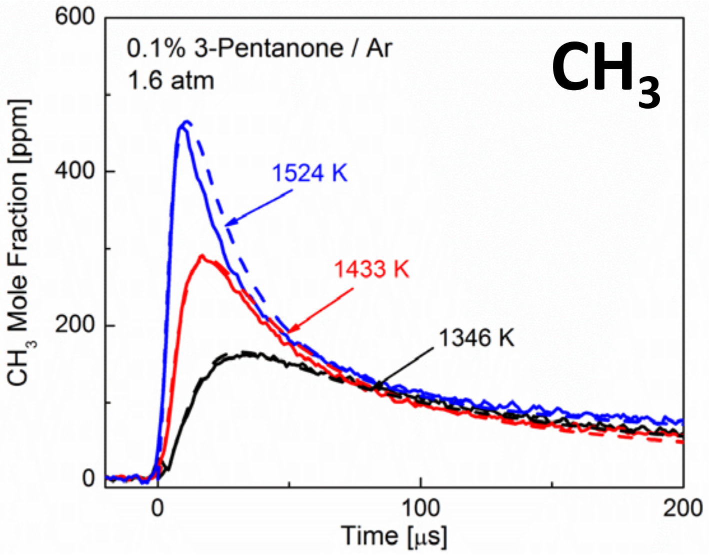
3-Pentanone:	**23%**
CO:	**43%**
CH_3CHCO:	**27%**
Sum:	**93%**

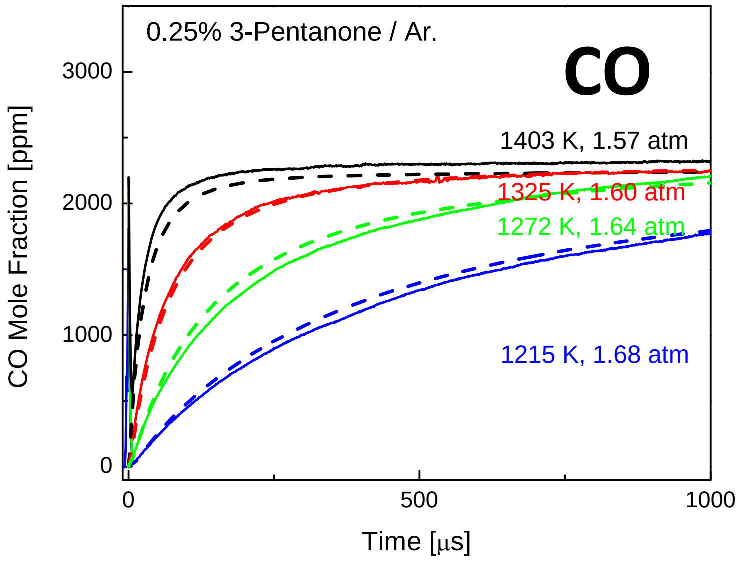
- **Model underpredicts CO and overpredicts methyl ketene**
- **Why? Methyl ketene decomposition pathway missing in mechanism**
- **Introduce $CH_3CHCO \rightarrow C_2H_4 + CO$ (assume *k* the same as ketene decomp.)**

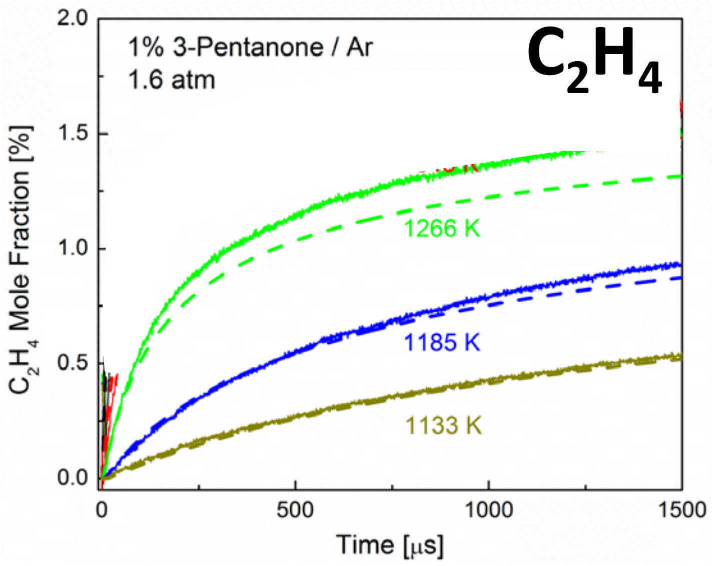
Revised Model Improves 3-P Simulations

Final Modifications to Serinyel et al. 3-Pentanone Mechanism

- **Revised decomposition rate:**
  3-pentanone → products
- **Additional reaction:**
  methylketene → $C_2H_4 + CO$







- **Good agreement with 3-P, CH_3, CO, and Low-T C_2H_4 time-histories**

Ongoing Work

- **Diagnostics development & spectroscopy:**
  - **aldehydes (CH_2O, CH_3CHO)**
  - **alkyl radicals (C_2H_5)**
  - **methyl esters (methyl formate)**
  - **Alkenes (C_3H_6, C_4H_8)**

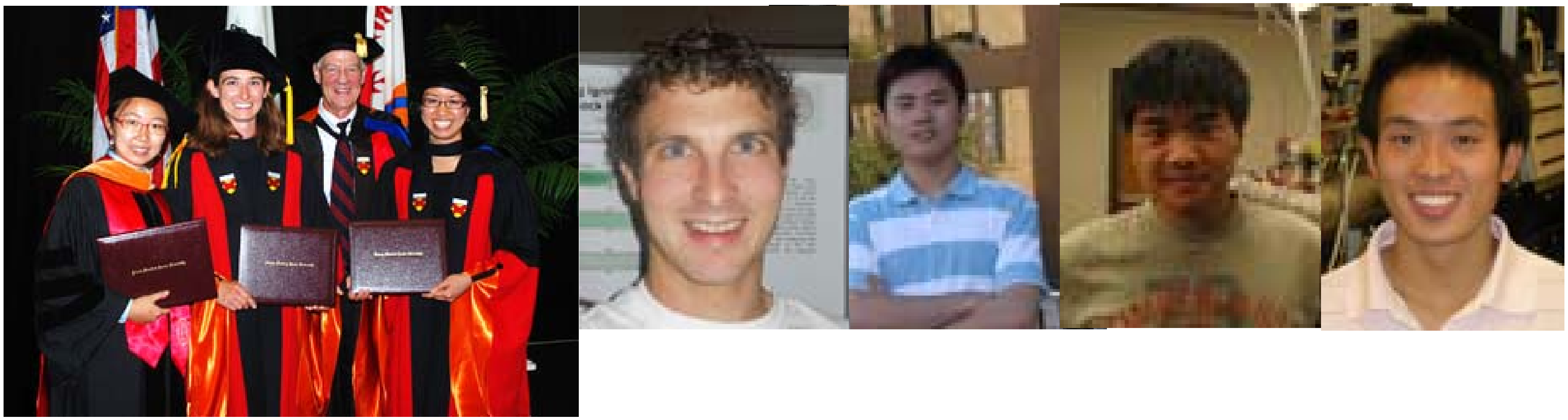
- **Continued improvement of shock tube methods:**
  - **constrained reaction volume**

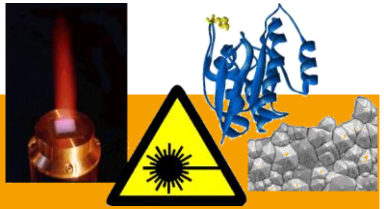
- **Direct measurement of elementary reactions:**
  - **OH + oxygenates (aldehydes, ethers, alcohols)**
  - **decomposition of oxygenates**
  - **CH_3, HO_2 reactions with HC**

Acknowledgements

- ARO, AFOSR, DOE, NSF

- Students:
- Genny Pang, Matt Campbell, Wei Ren, Brian Lam, Sijie Li, Sreyashi Chakraborty





The role of advanced diagnostics in combustion *chemistry* research

Katharina Kohse-Höinghaus

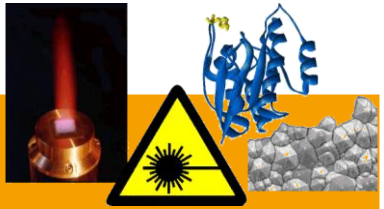
Bielefeld University, Germany

Fei Qi

USTC, China

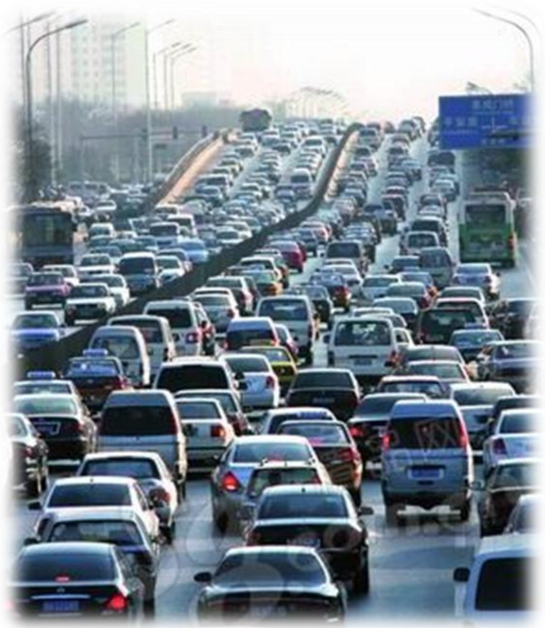
Nils Hansen

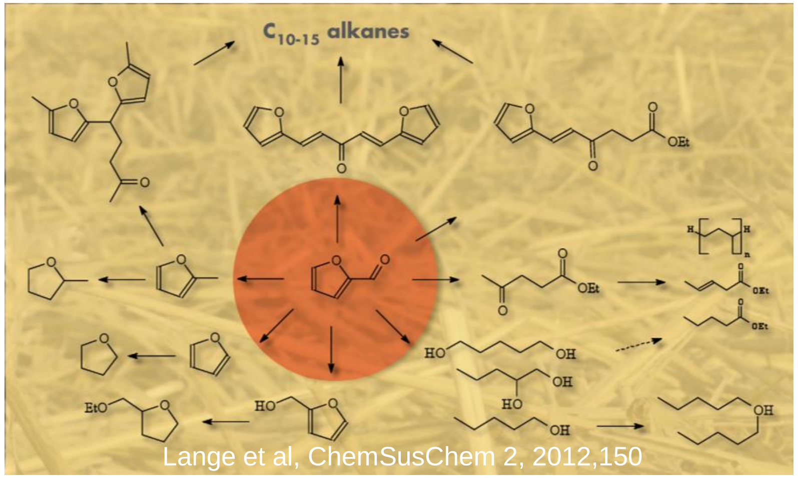
Sandia National Lab, USA



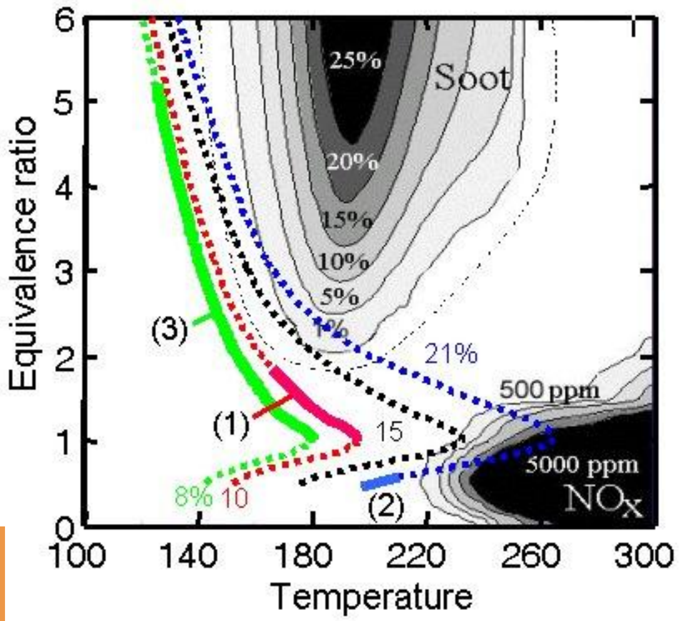
Introduction: The problem

- ➢**Clean combustion: high efficiency, low emissions**
- ➢**Alternative transportation fuels: new chemistry**
- ➢**Novel combustion regimes: influences of p, T, phi, mixture**

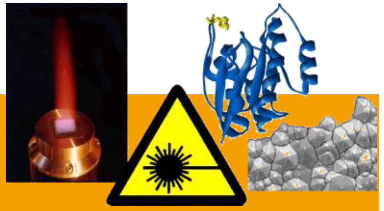




Lange et al, ChemSusChem 2, 2012,150

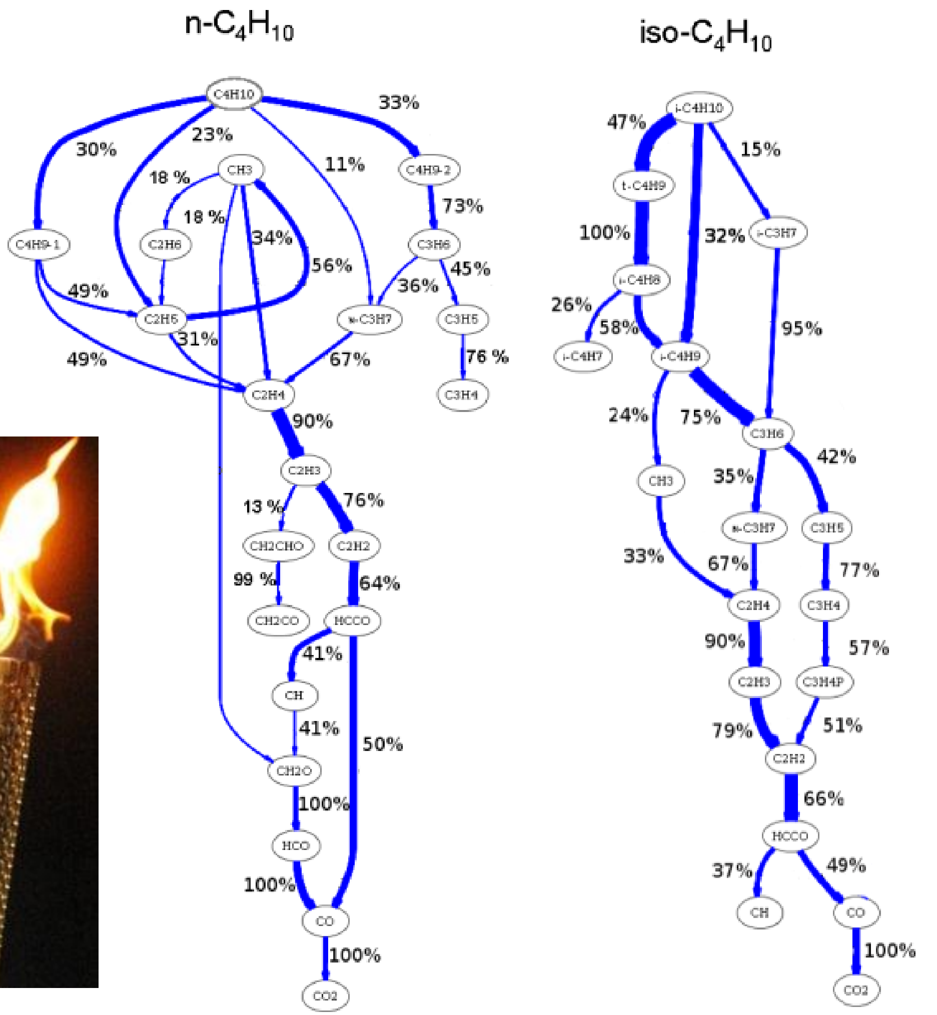


Needed: Systematic knowledge on combustion chemistry

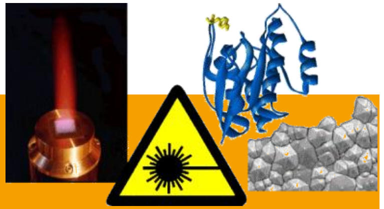


Probing flame chemistry: Wanted

- ➢**In situ information on unknown species mix: identification.**
- ➢**Large dynamic range of mole fractions, labile species.**
- ➢**Quantitative set of concentration-reaction time profiles.**
- ➢***Example*: butane combustion, ~ 40 species.**

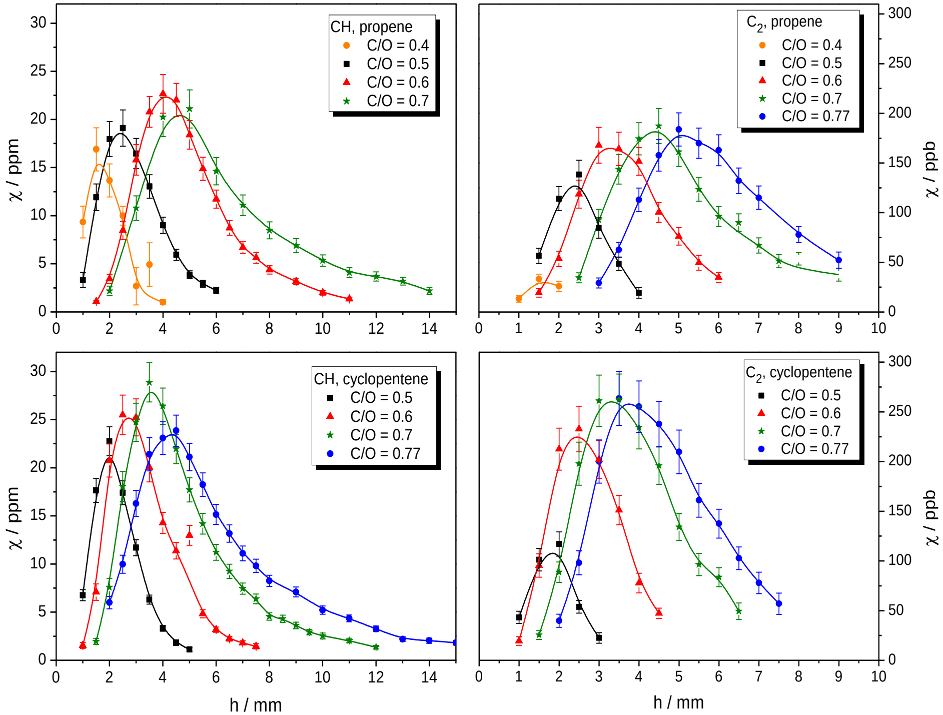

n-C_4H_{10}
C4H10
33%
30%
23%
11%
CH3
C4H9-2
18 %
18 %
73%
C4H9-1
C2H6
34%
C3H6
56%
45%
49%
36%
C2H5
n-C3H7
C3H5
31%
49%
67%
76 %
C2H4
C3H4
90%
C2H3
13 %
76%
CH2CHO
C2H2
99 %
64%
CH2CO
HCCO
41%
CH
41%
50%
CH2O
100%
HCO
100%
CO
100%
CO2
iso-C_4H_{10}
i-C4H10
47%
15%
t-C4H9
100%
32%
i-C3H7
i-C4H8
26%
58%
95%
i-C4H7
i-C4H9
24%
75%
C3H6
42%
CH3
35%
n-C3H7
C3H5
33%
67%
77%
C2H4
C3H4
90%
57%
C2H3
C3H4P
79%
51%
C2H2
66%
HCCO
37%
49%
CH
CO
100%
CO2

Oßwald et al, Z Phys Chem 225, 2011,1029

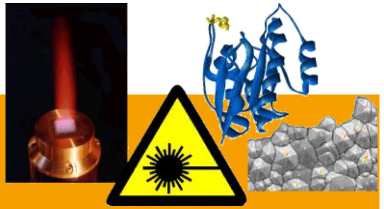


Probing flame chemistry: laser diagnostics

- **Laser spectroscopy: Raman, LIF, CRDS, IR absorption, etc.**
- **Quantitative, non-intrusive, *small* molecules: *e.g.* CH, C_2**
- **Not suitable for complete flame analysis**

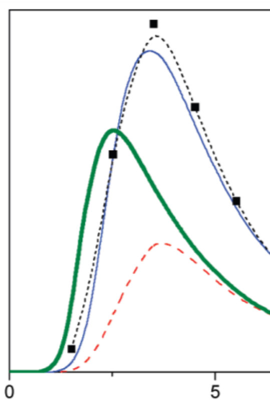


M. Köhler et al, J Phys Chem A114, 2010, 4719



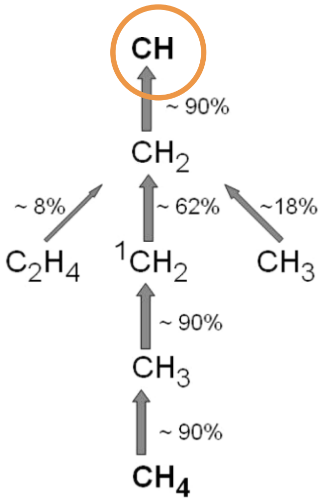
Small species and chemical mechanisms

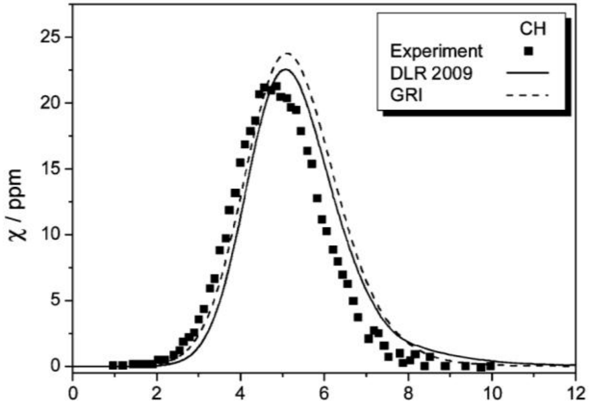
- ➢One species ***cannot*** validate mechanisms.
- ➢Small species are at ***end*** of reaction chain.

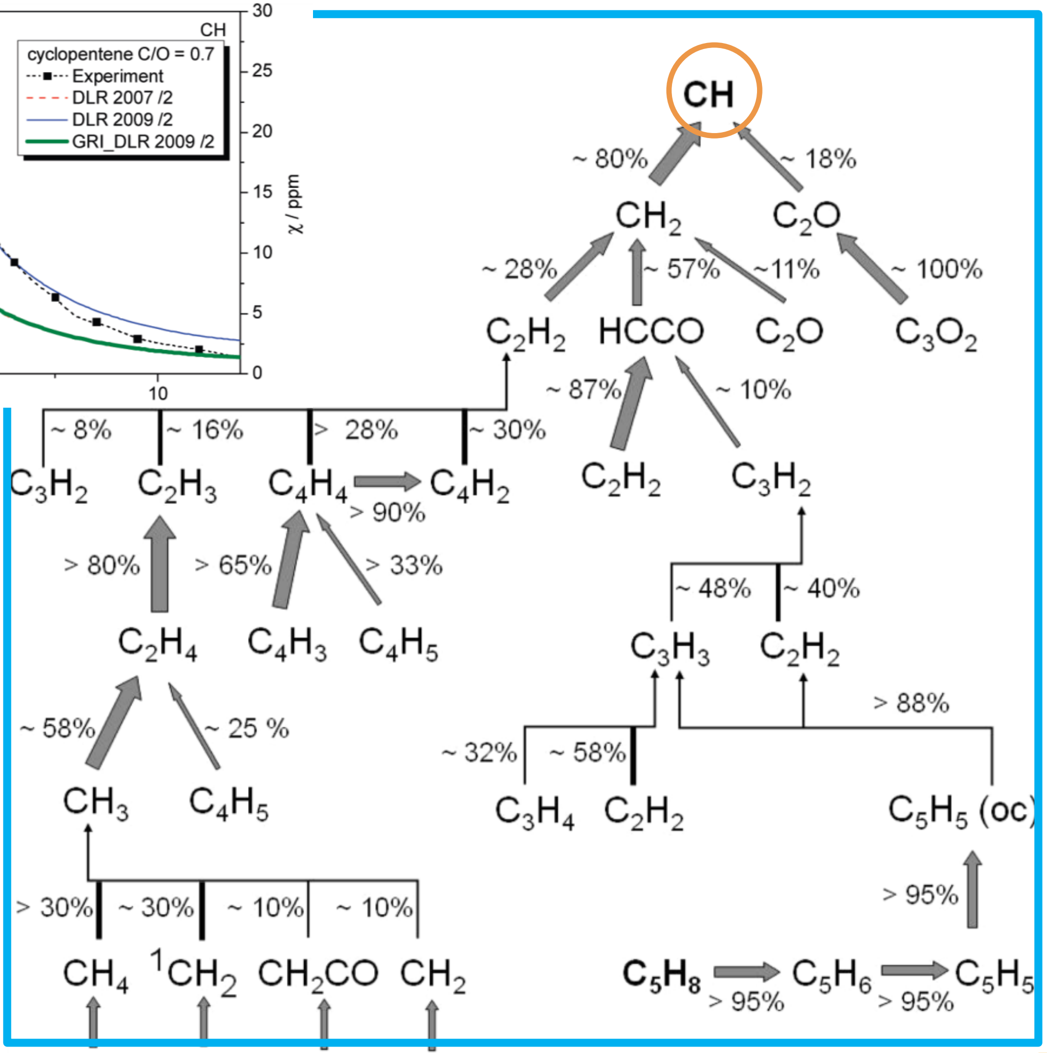


← **methane**

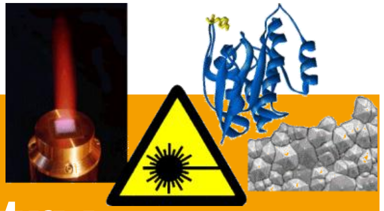
cyclopentene →


CH
~ 90%
CH2
~ 8%
~ 62%
~18%
C2H4
1CH2
CH3
~ 90%
CH3
~ 90%
CH4



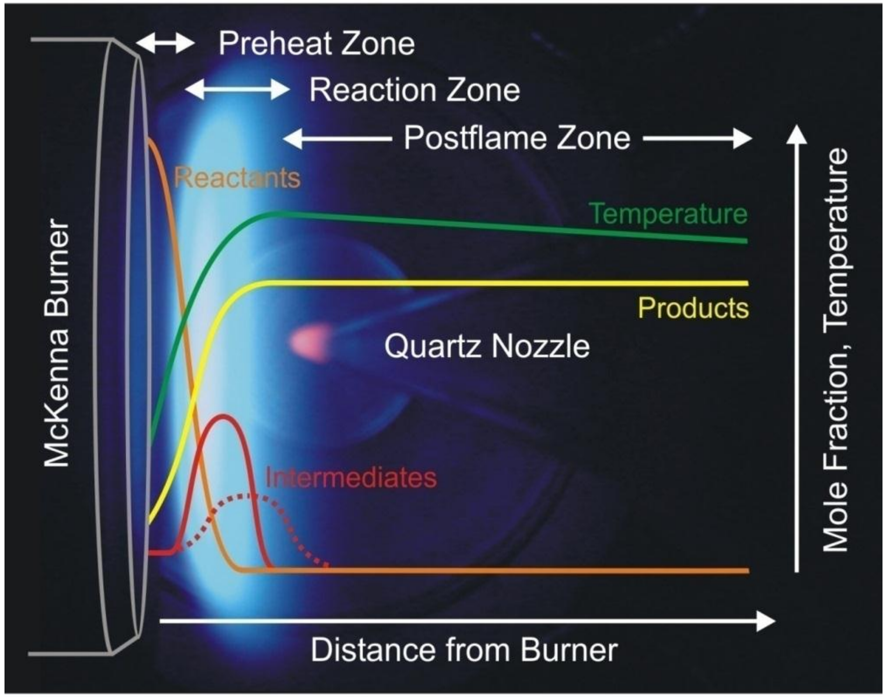

CH
~ 80%
~ 18%
CH2
C2O
~ 28%
~ 57%
~11%
~ 100%
C2H2
HCCO
C2O
C3O2
~ 87%
~ 10%
~ 8%
~ 16%
> 28%
~ 30%
C3H2
C2H3
C4H4
C4H2
C2H2
C3H2
> 90%
> 80%
> 65%
> 33%
~ 48%
~ 40%
C2H4
C4H3
C4H5
C3H3
C2H2
~ 58%
~ 25 %
> 88%
~ 32%
~ 58%
CH3
C4H5
C3H4
C2H2
C5H5 (oc
> 30%
~ 30%
~ 10%
~ 10%
> 95%
CH4
1CH2
CH2CO
CH2
C5H8
C5H6
C5H5
> 95%
> 95%

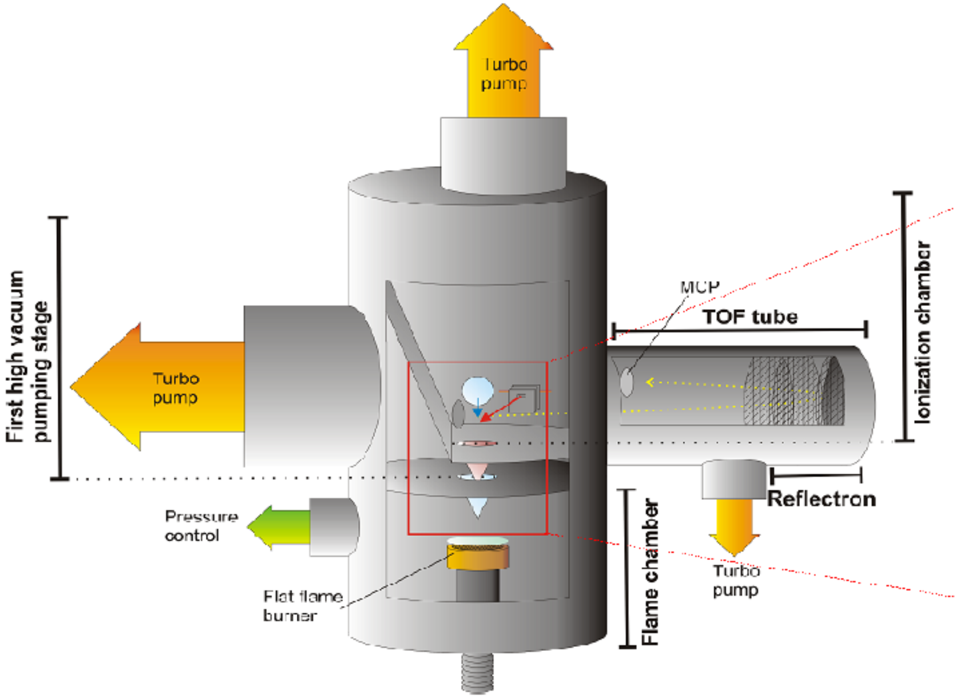
M. Köhler et al, J Phys Chem A114, 2010, 4719

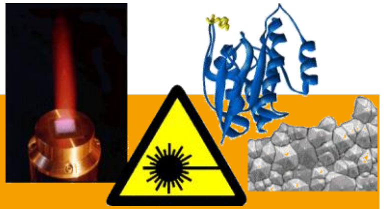


Probing flame chemistry: mass spectrometry

- **Molecular-beam mass spectrometry (MBMS):**
- ***Complete*** **species set (?!); structure-sensitive, isomers**
- **Quantitative – *but*: fragmentation, overlaps, sampling, ….**

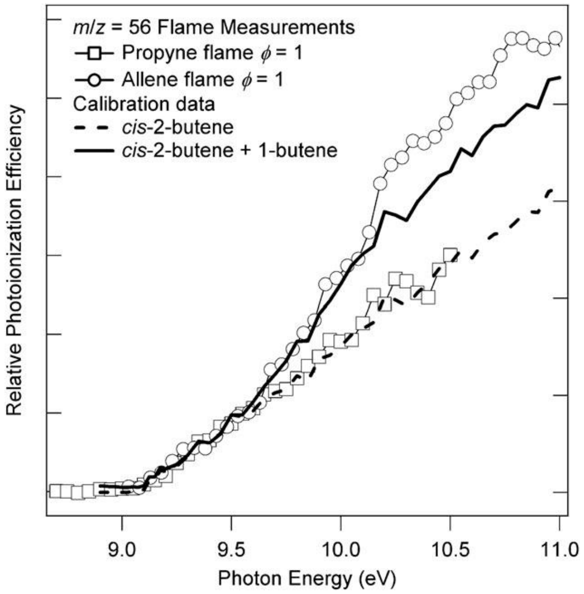

Preheat Zone
Reaction Zone
Postflame Zone
Reactants
Temperature
Products
Quartz Nozzle
McKenna Burner
Intermediates
Mole Fraction, Temperature
Distance from Burner


Turbo pump
First high vacuum pumping stage
Turbo pump
Pressure control
Flat flame burner
Flame chamber
MCP
TOF tube
Ionization chamber
Reflectron
Turbo pump

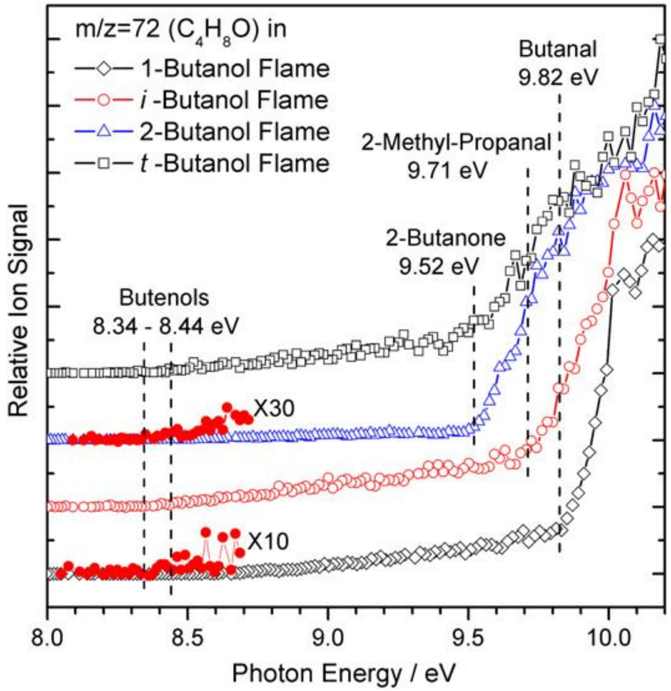


Species- and structure-selective analysis

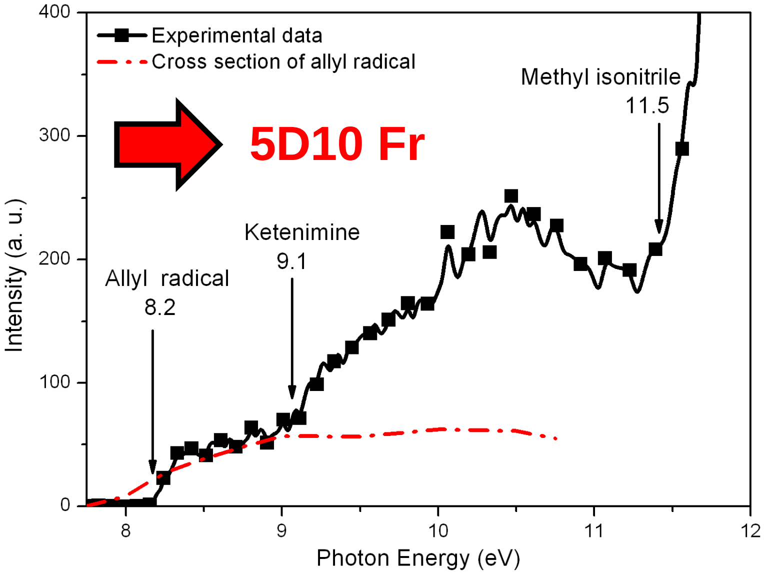
- ➢**Tunable VUV single-photon PI-MBMS:**
- ➢**Distinction of intermediates in C/H, C/H/O, and C/H/O/N systems**
- ➢**Mass & photoionization efficiency (PIE) spectra as discriminators**



C.A. Taatjes et al, PCCP 10, 2008, 1

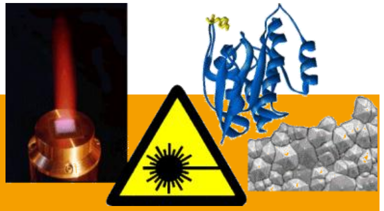


B. Yang et al, Combust Flame 148, 2007,198



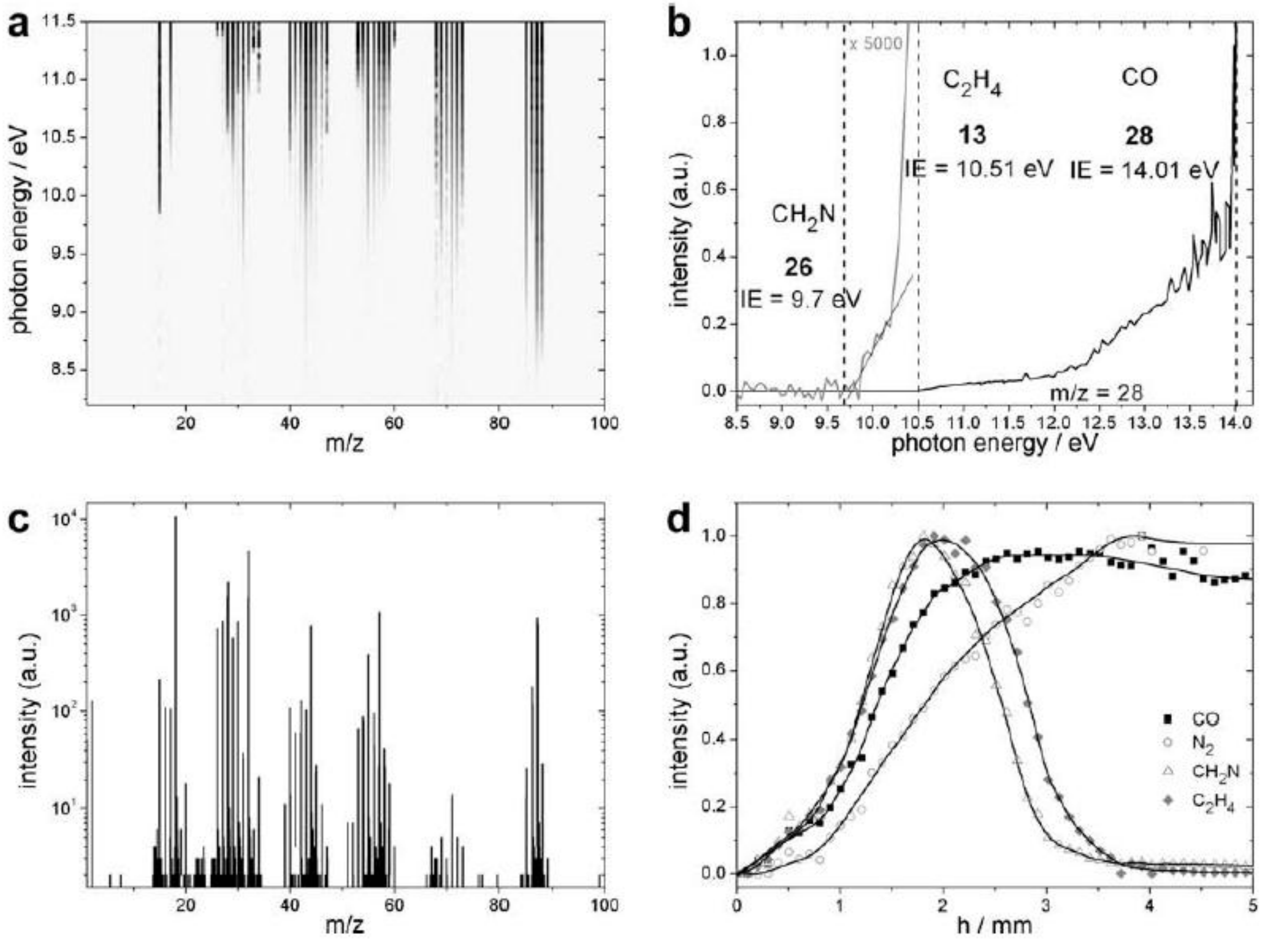
m/z=41, C_3H_5, C_2H_2NH, CH_3NC (CH_3CN)

A. Lucassen et al, PROCI 34, 2012

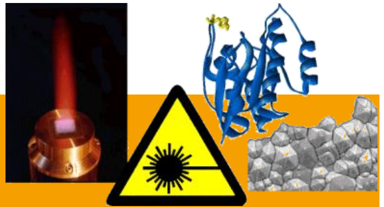


Combining high mass + energy resolution

- ➢**Fuel complexity: hydrocarbons → oxygenates → fuel-N.**
- ➢**More elements need better *mass separation:* →EI-MBMS.**
- ➢**Fuel structure and intermediate mix need *isomer separation:* →PI-MBMS.**
- ➢***Example:* morpholine flame.**

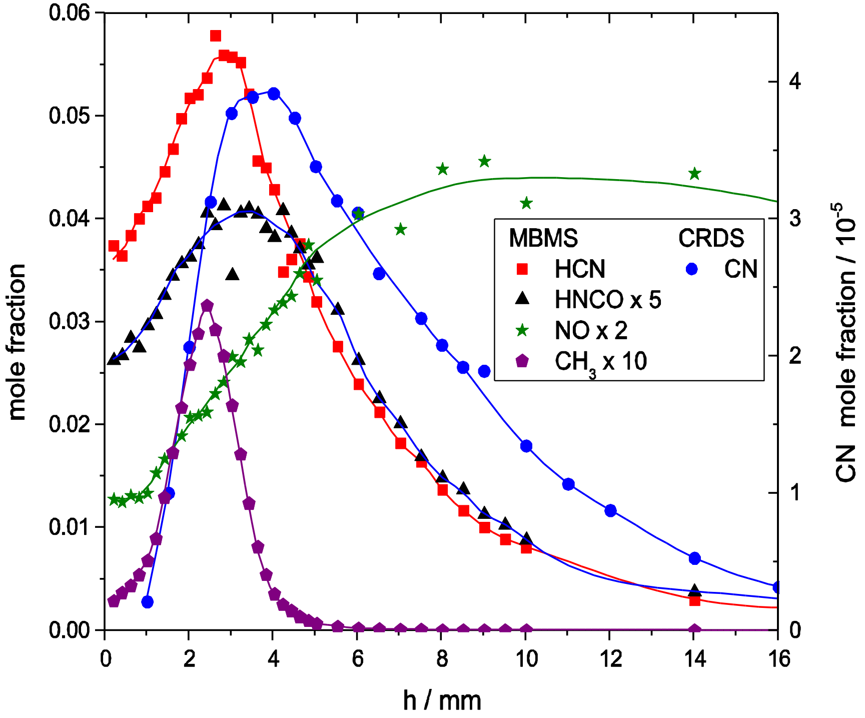


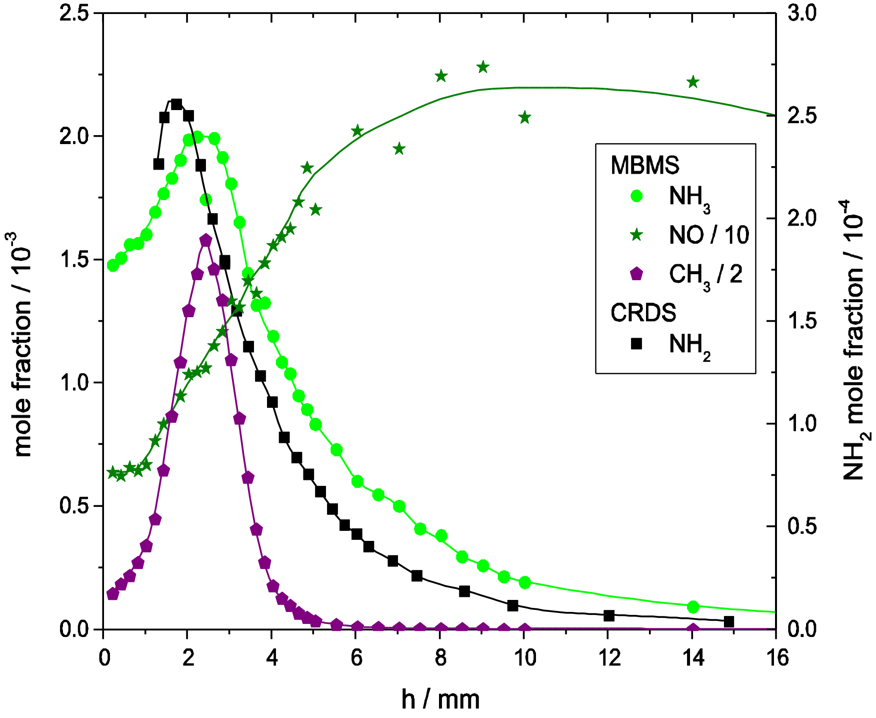
A. Lucassen et al, PROCI 32, 2009,1269



Combining EI-MBMS+PI-MBMS+LIF+CRDS

- MBMS results for HCN, NH_3, NO, HNCO, CH_3, ...
- LIF temperature measurement
- CRDS results for NH_2, CN, CH, OH, …

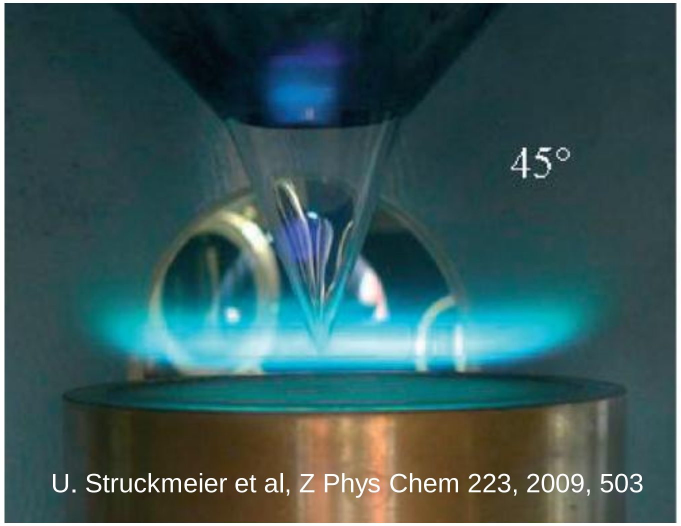




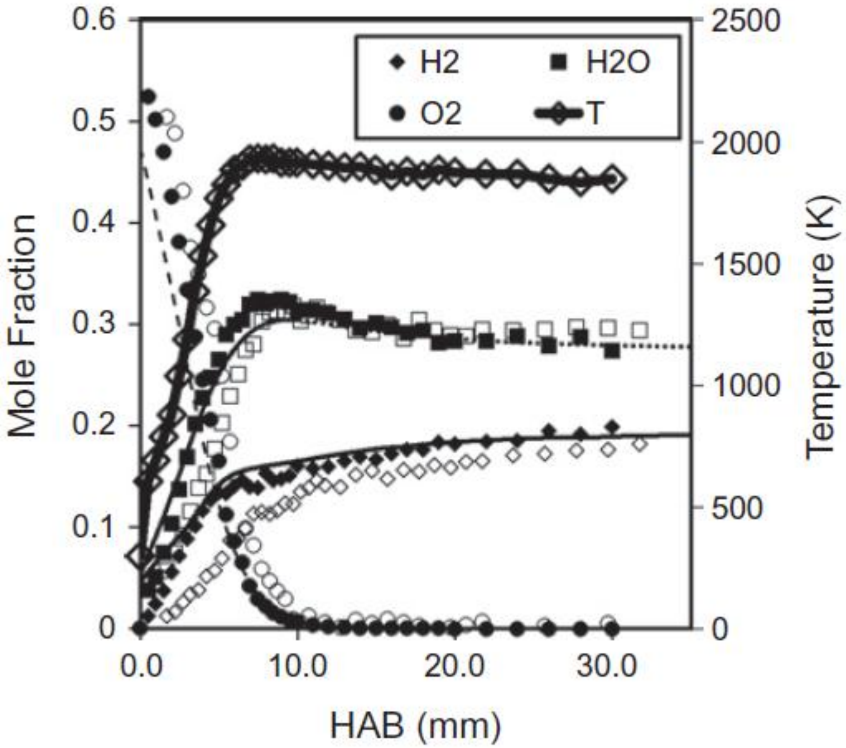
P. Nau et al, Exp Fluids 32, 2009,1269

Experiment vs. model: (un)disturbed T profile

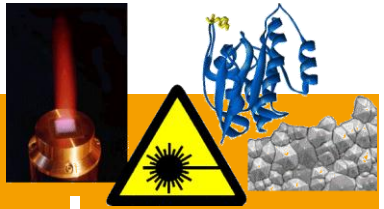
- ➢***T profile*** **for optical or MBMS sampling must be considered in comparison with models – no shifts!**
- ➢***Example:*** **butanol flames.**



U. Struckmeier et al, Z Phys Chem 223, 2009, 503

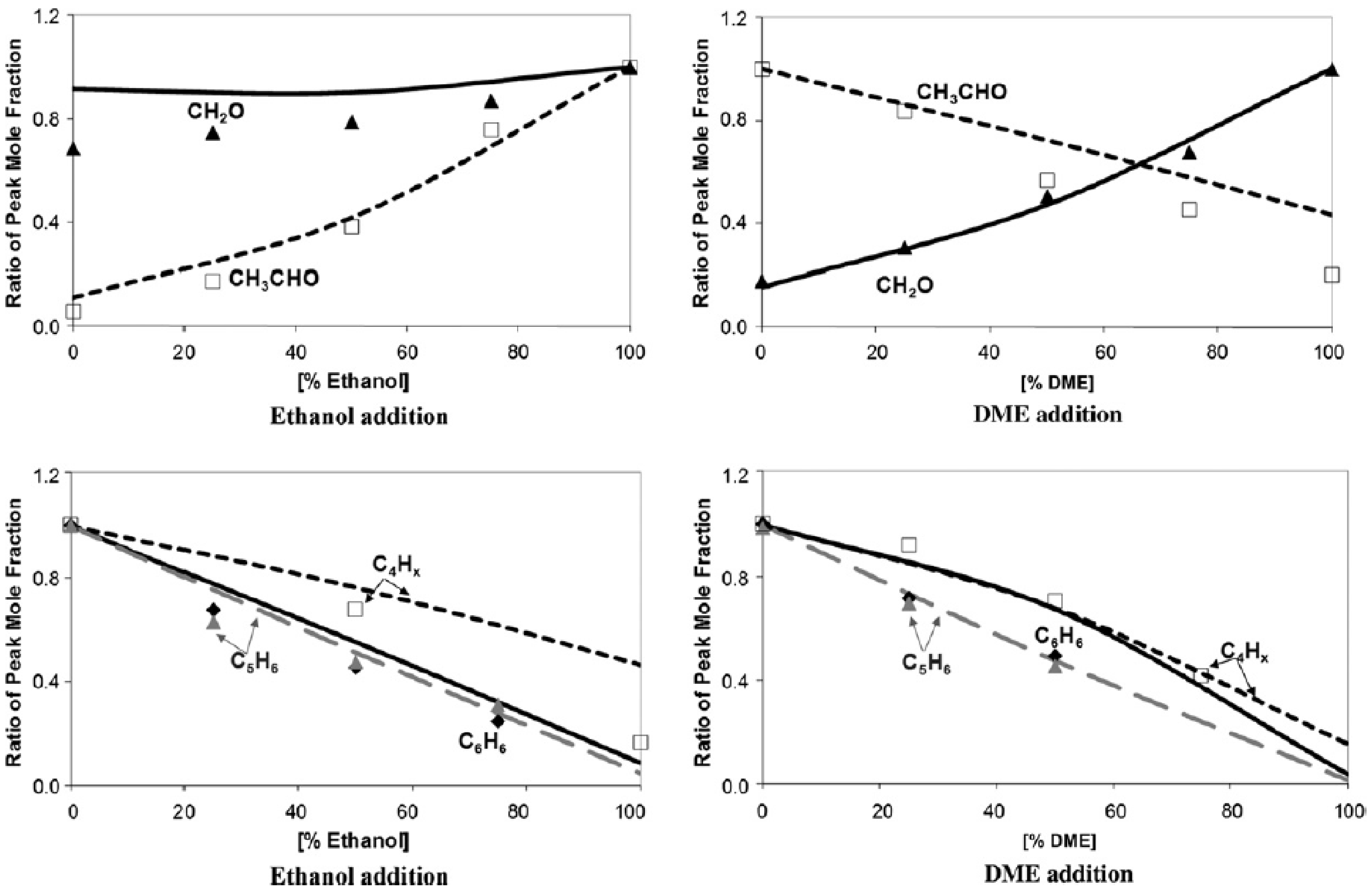


M. Sarathy et al, Combust Flame 159, 2012, 2028

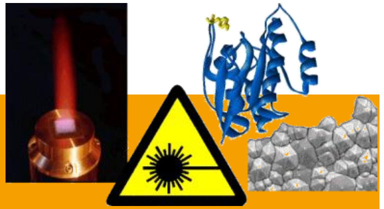


New combustion details: study of isomeric fuels

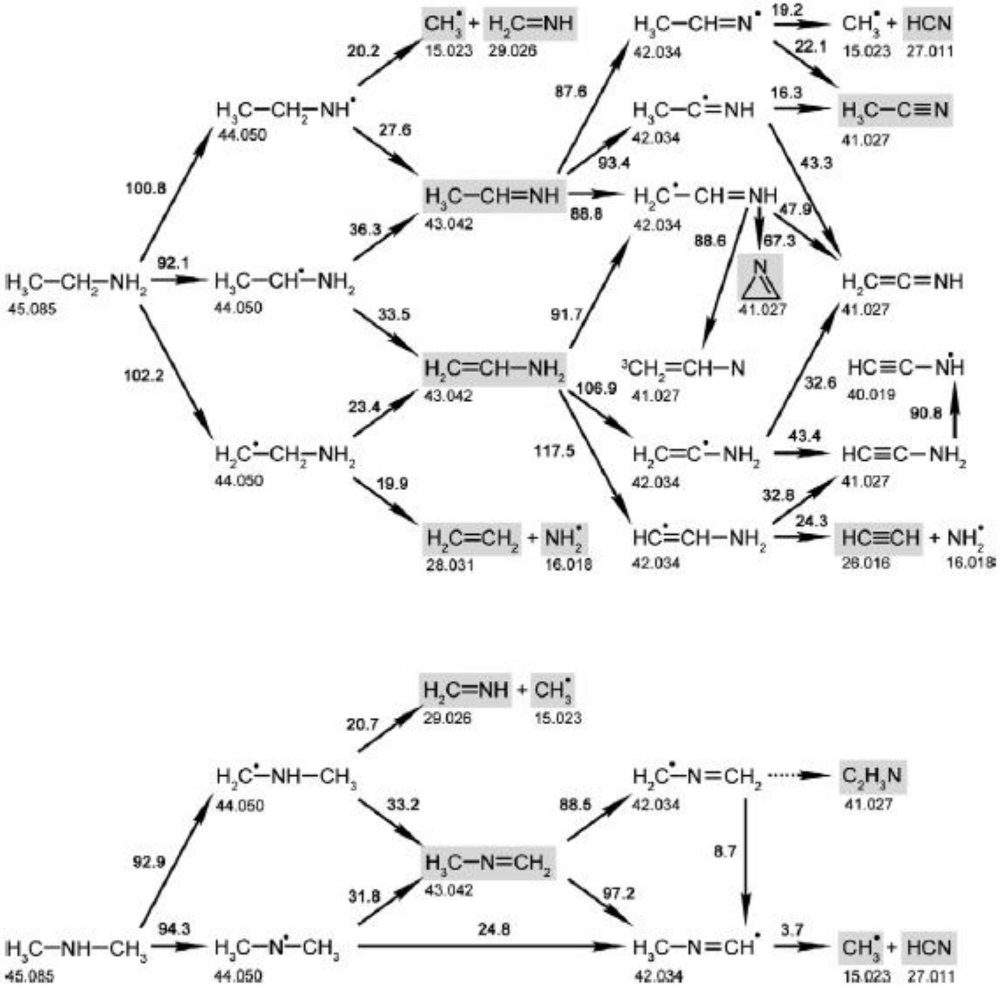
- **Quantitative but *relative* species measurement is more forgiving.**
- **Chemical trends are more obvious.**
- **Model can probe mechanistic differences.**
- ***Example:* ethanol and DME addition to propene.**



A. Frassoldati et al, Combust Flame 158, 2011, 1264

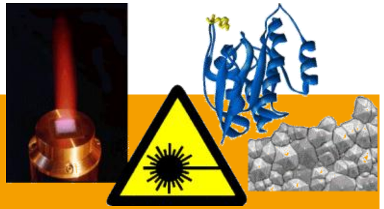


Fuel-N conversion: biomass components

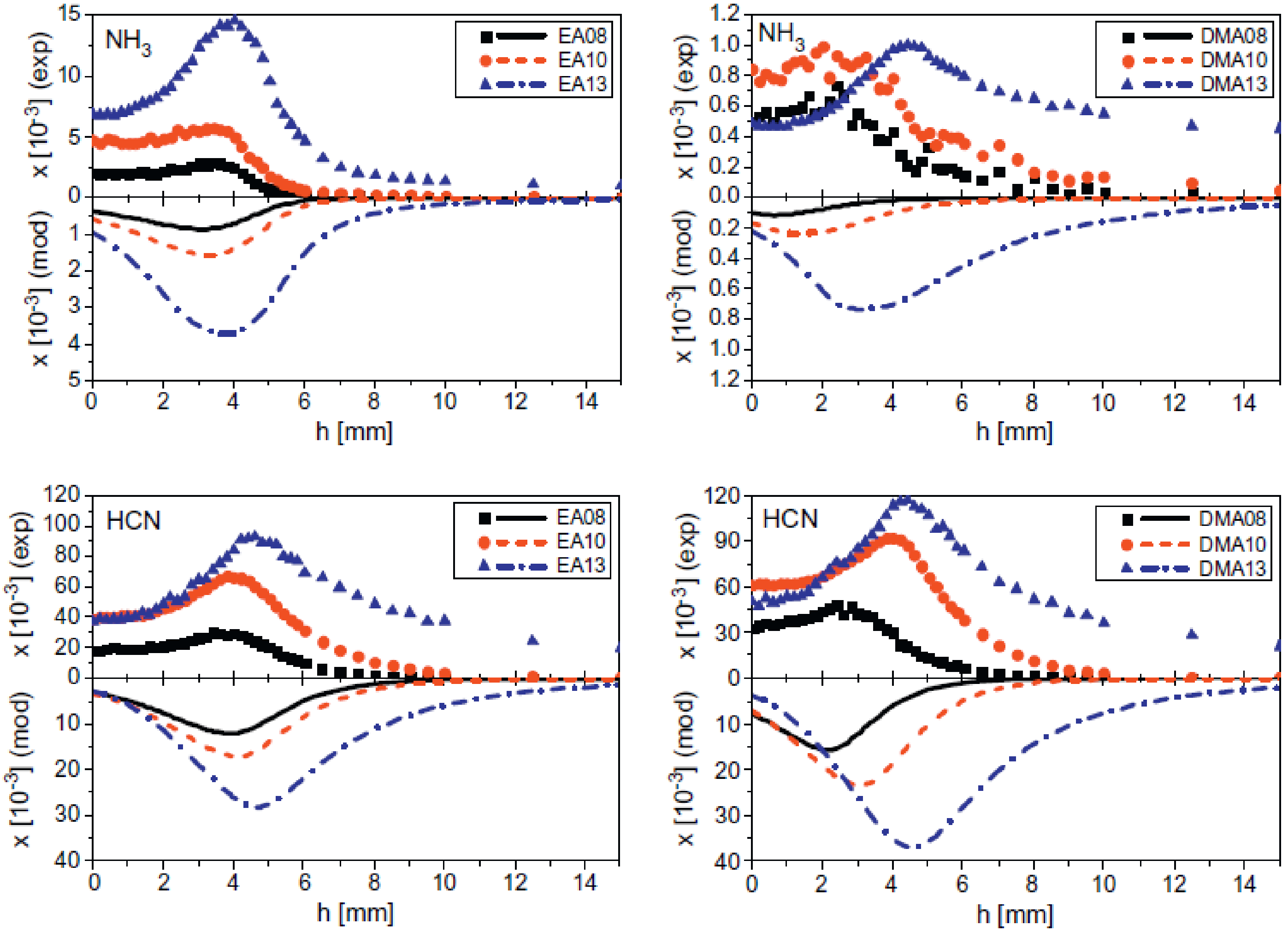

$H_3C{-}CH_2{-}NH_2$
45.085
100.8
92.1
102.2
$H_3C{-}CH_2{-}NH^\bullet$
44.050
$H_3C{-}CH^\bullet{-}NH_2$
44.050
$H_2C^\bullet{-}CH_2{-}NH_2$
44.050
20.2
27.6
36.3
33.5
23.4
19.9
$CH_3^\bullet + H_2C{=}NH$
15.023 29.026
$H_3C{-}CH{=}NH$
43.042
$H_2C{=}CH{-}NH_2$
43.042
$H_2C{=}CH_2 + NH_2^\bullet$
28.031 16.018
87.6
93.4
88.8
91.7
106.9
117.5
$H_3C{-}CH{=}N^\bullet$
42.034
$H_3C{-}C^\bullet{=}NH$
42.034
$H_2C^\bullet{-}CH{=}NH$
42.034
88.6
67.3
N
41.027
$^3CH_2{=}CH{-}N$
41.027
$H_2C{=}C^\bullet{-}NH_2$
42.034
$HC^\bullet{=}CH{-}NH_2$
42.034
19.2
22.1
16.3
43.3
47.9
32.6
43.4
32.8
24.3
90.8
$CH_3^\bullet + HCN$
15.023 27.011
$H_3C{-}C{\equiv}N$
41.027
$H_2C{=}C{=}NH$
41.027
$HC{\equiv}C{-}NH^\bullet$
40.019
$HC{\equiv}C{-}NH_2$
41.027
$HC{\equiv}CH + NH_2^\bullet$
26.016 16.018
$H_3C{-}NH{-}CH_3$
45.085
92.9
94.3
$H_2C^\bullet{-}NH{-}CH_3$
44.050
$H_3C{-}N^\bullet{-}CH_3$
44.050
20.7
33.2
31.8
24.8
$H_2C{=}NH + CH_3^\bullet$
29.026 15.023
$H_3C{-}N{=}CH_2$
43.042
88.5
97.2
$H_2C^\bullet{-}N{=}CH_2$
42.034
8.7
$H_3C{-}N{=}CH^\bullet$
42.034
3.7
C_2H_3N
41.027
$CH_3^\bullet + HCN$
15.023 27.011

A. Lucassen et al, Combust Flame 159, 2012, 2254

- ➢***Isomeric*** **fuel decomposition pathways different.**
- ➢**Ethylamine break-down suggests early NH_3 formation.**
- ➢**Substantial HCN mole fractions expected for both fuels.**
- ➢***Example:*** **ethylamine and dimethylamine combustion.**

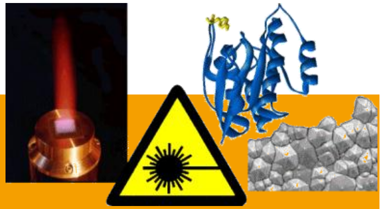


Ethylamine vs. dimethylamine combustion

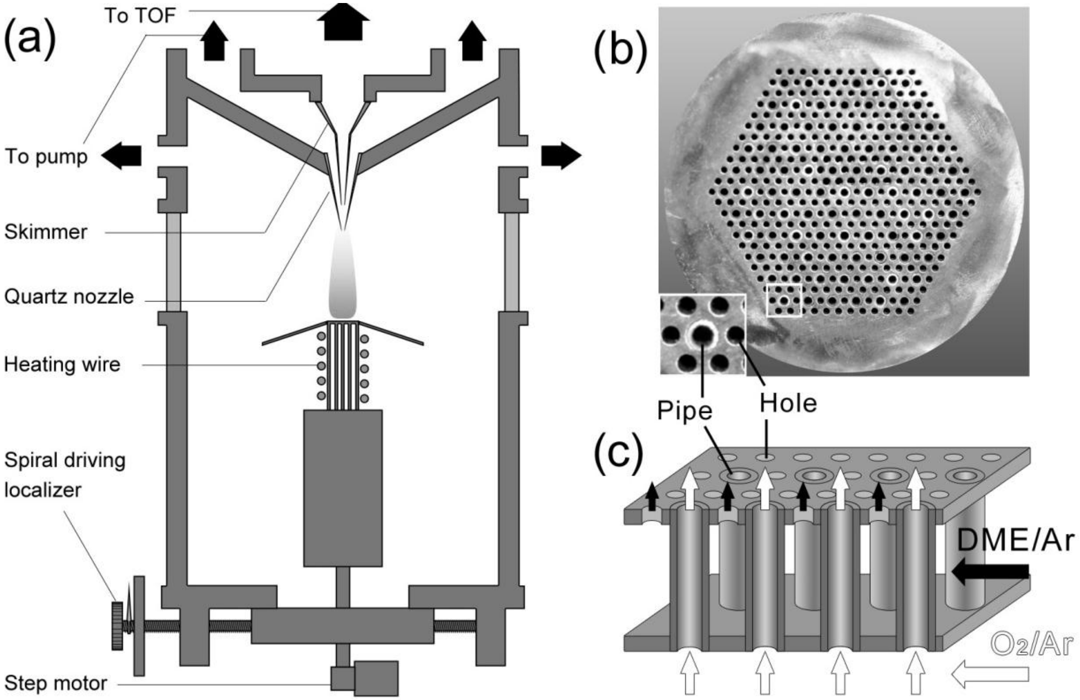


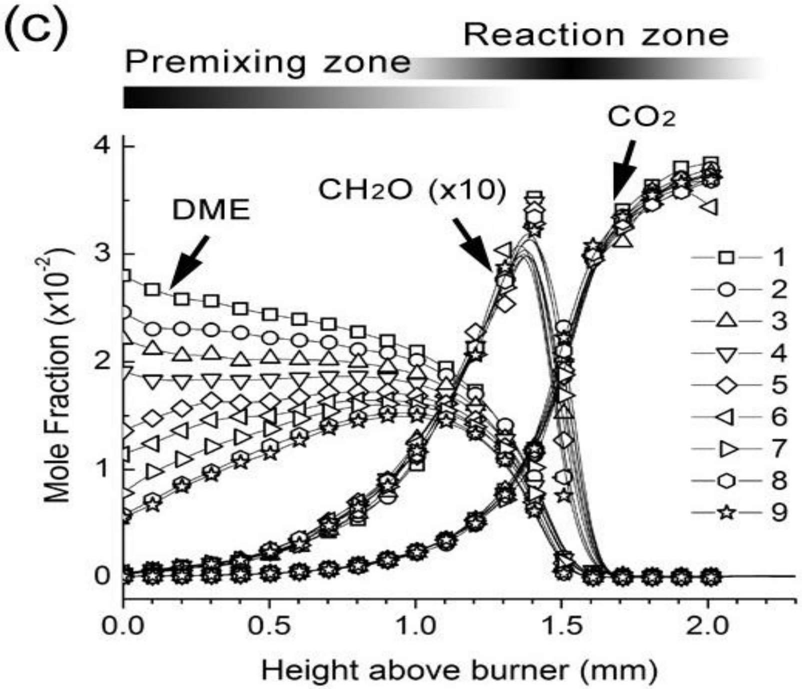
A. Lucassen et al, Combust Flame 159, 2012, 2254

- NH$_3$ mole fractions much higher for EA.
- Model under-predicts NH$_3$ in both flame sets.
- High HCN mole fractions of up to 12%.
- Model under-predicts HCN.



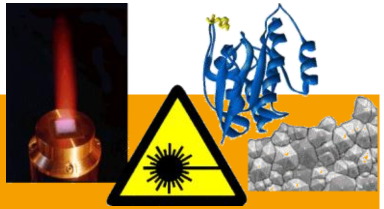
Low-temperature combustion chemistry


(a)
To TOF
To pump
Skimmer
Quartz nozzle
Heating wire
Spiral driving
localizer
Step motor
(b)
Pipe
Hole
(c)
DME/Ar
O2/Ar

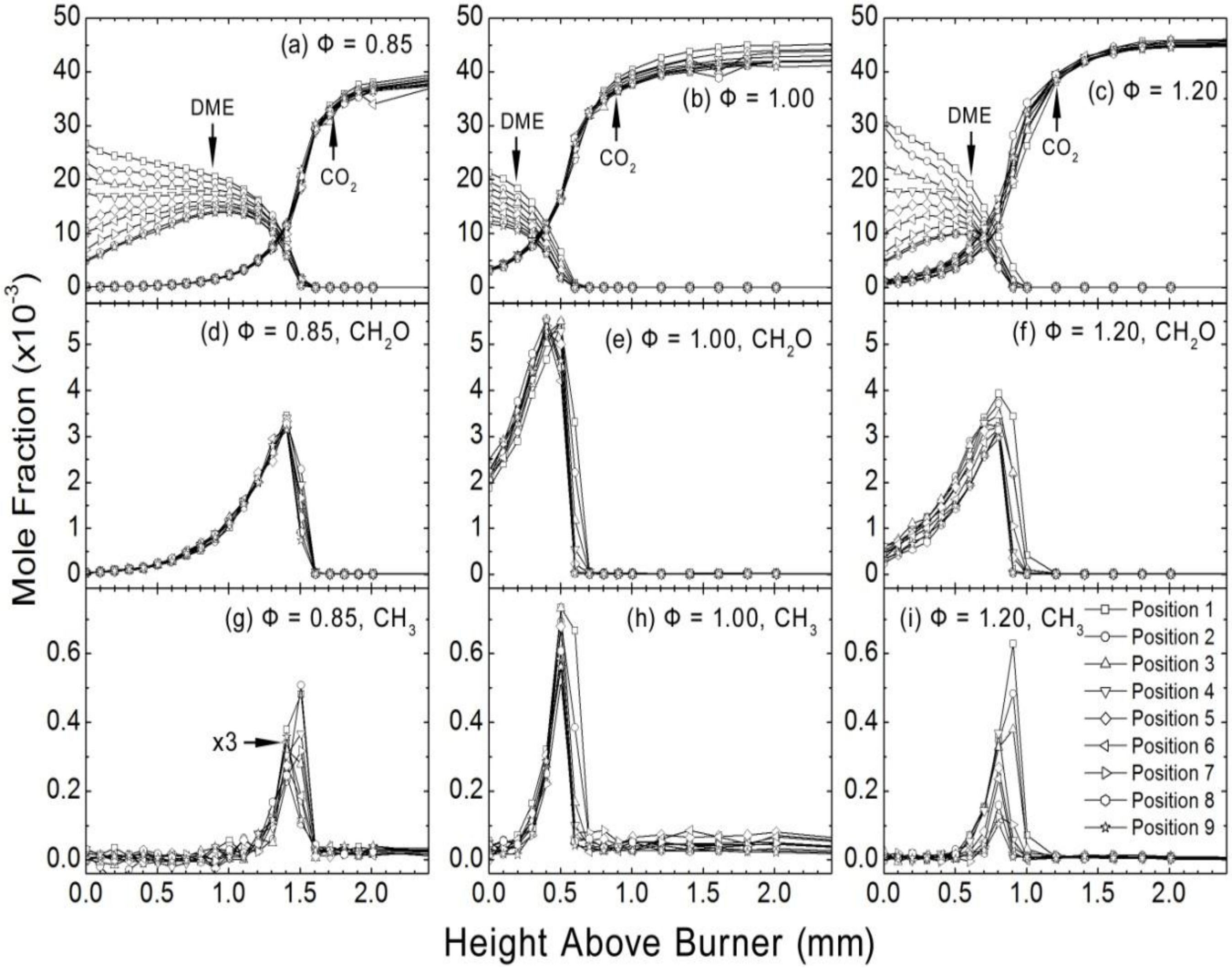


- ➢**Sampling from highly-diluted, preheated, partially-premixed DME flame at 1 bar with T = 1400 K.**
- ➢**Partially-premixing species profiles are *position*-dependent.**

K. Zhang et al, PROCI 34, 2012



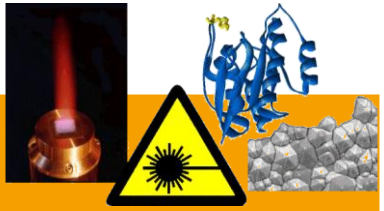
Low-temperature combustion chemistry



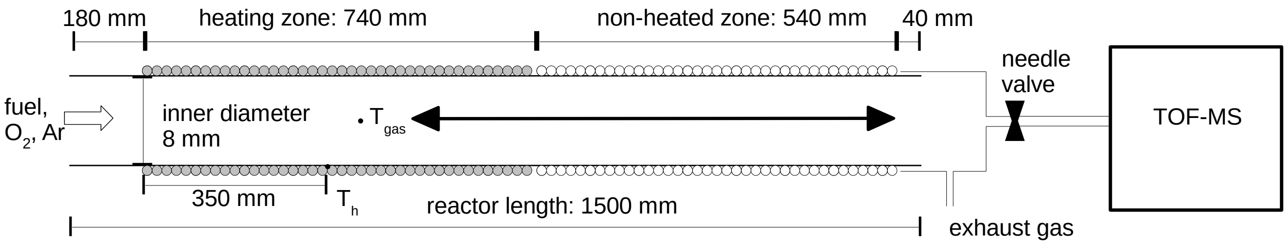
- **Highly diluted preheated DME combustion.**
- **Three stoichiometries: 0.85, 1.0, and 1.2. *Intermediate-T* behavior; e.g. CH_3 vs. CH_2O.**

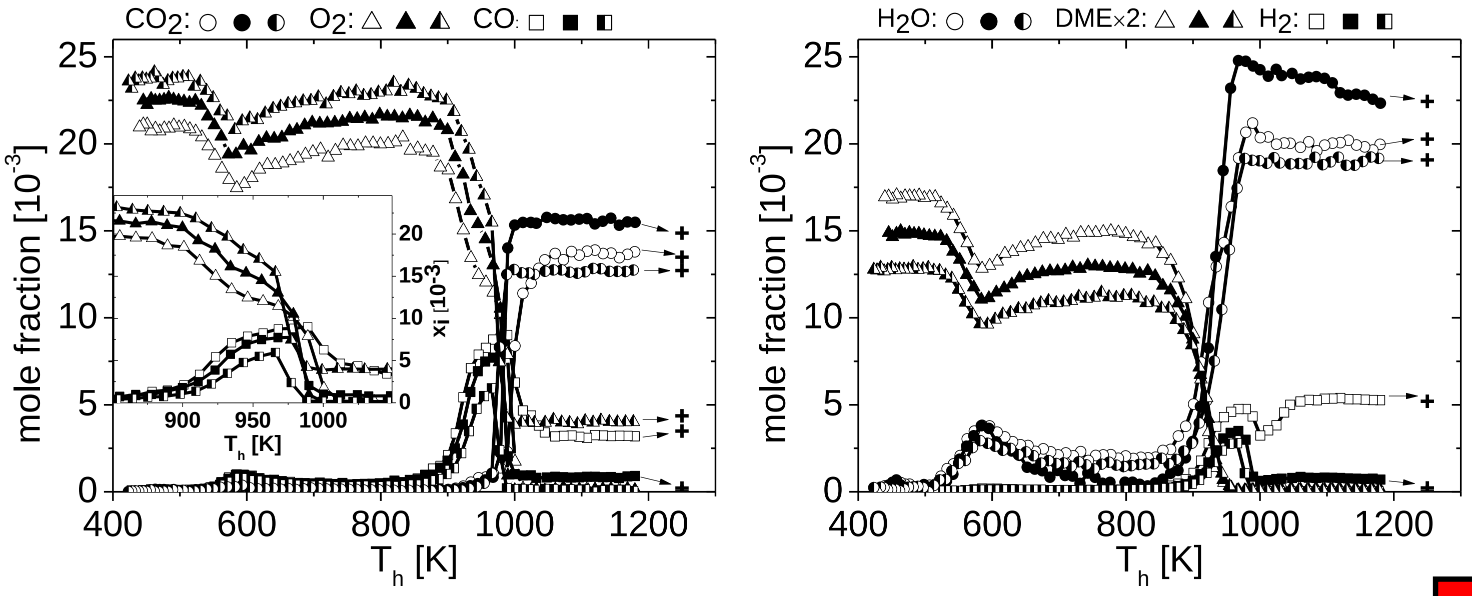
➡ 1E06 Mon

K. Zhang et al, PROCI 34, 2012



Low-temperature combustion chemistry

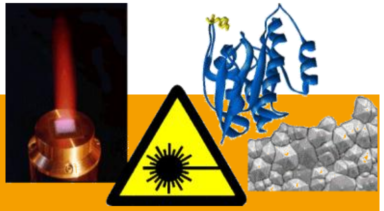

180 mm
heating zone: 740 mm
non-heated zone: 540 mm
40 mm
needle valve
TOF-MS
fuel, O_2, Ar
inner diameter 8 mm
T_{gas}
350 mm
T_h
reactor length: 1500 mm
exhaust gas



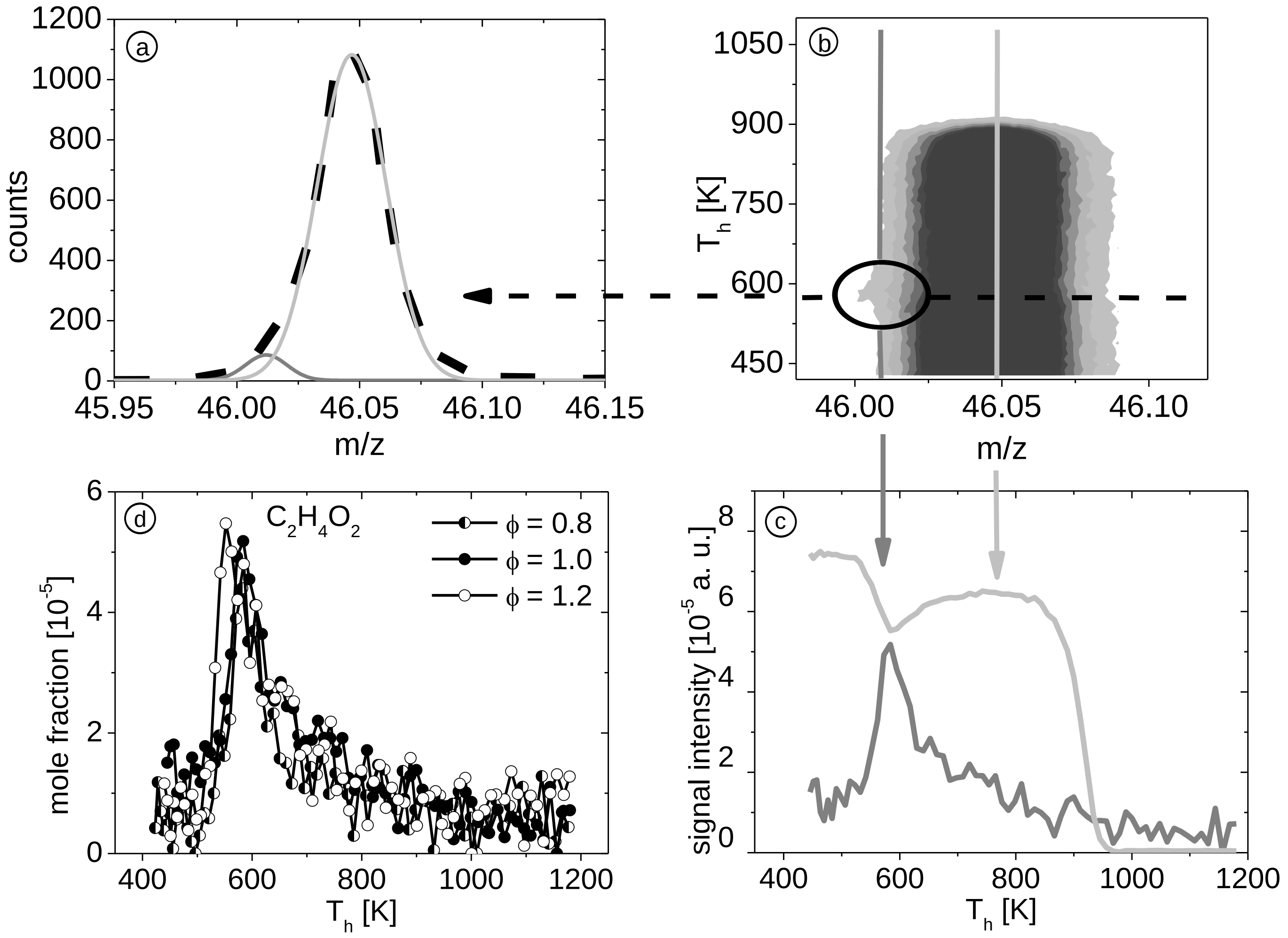
F. Herrmann et al, PROCI 34, 2012

- ➢**Highly diluted DME oxidation in flow reactor.**
- ➢**Three stoichio-metries: 0.8, 1.0, and 1.2. *Expected* low-T behavior.**
- ➢**Compare with model/ to EtOH: →WIP!**

1E07 Mon, W5P070 Fri



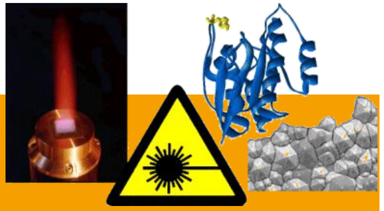
Low-temperature combustion chemistry



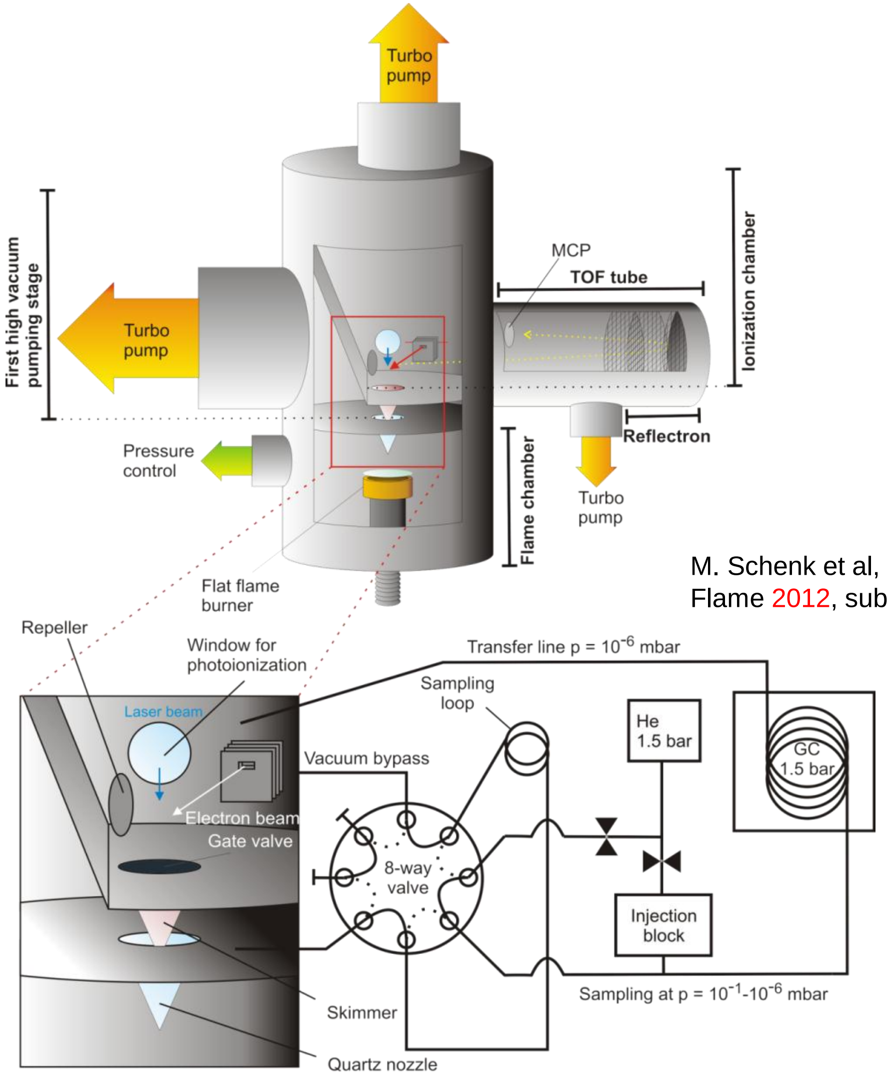
F. Herrmann et al, PROCI 34, 2012

- ➢DME oxidation in low-T flow reactor.
- ➢High mass resolution: fuel DME (46.042) and *formic acid* (46.010) at T_h = 583 K are separated.
- ➢*Methyl formate* is detected.
- ➢More species, VUV-PI-MBMS: →WIP!

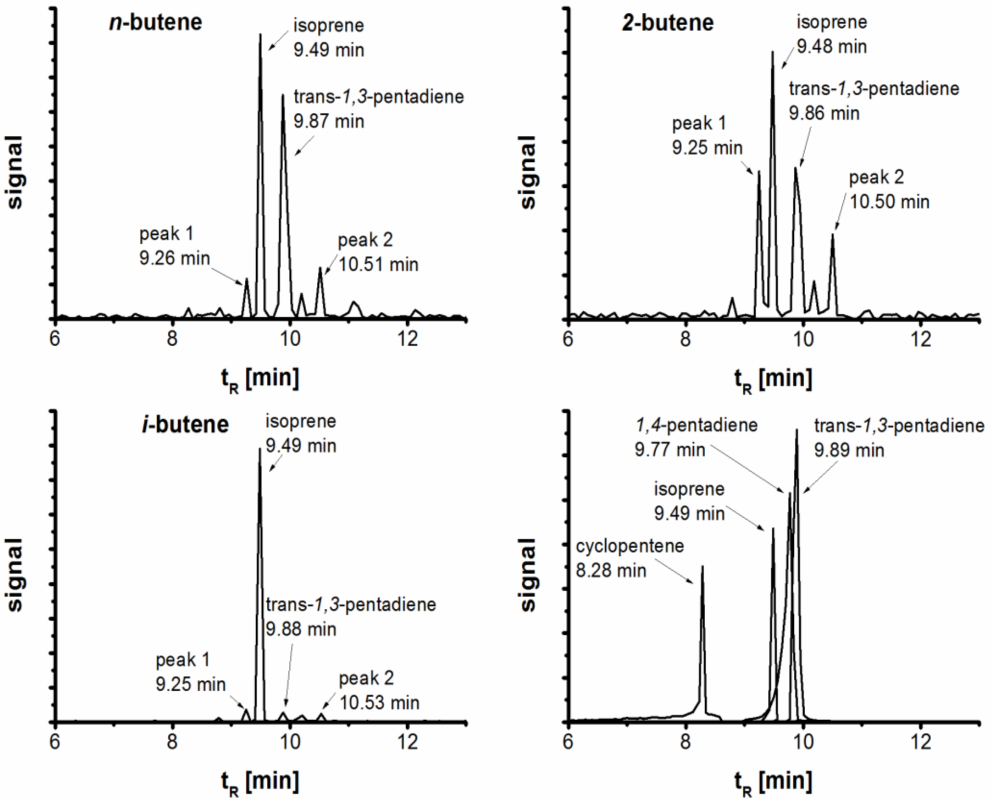
1E07 Mon, W5P072 Fri



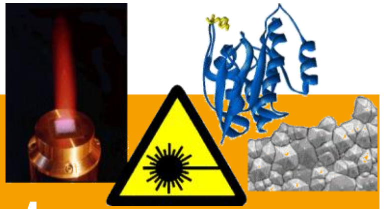
EI-MBMS and GC from the same volume


Turbo pump
First high vacuum pumping stage
Turbo pump
MCP
TOF tube
Ionization chamber
Reflectron
Pressure control
Flame chamber
Turbo pump
Flat flame burner
Repeller
Window for photoionization
Laser beam
Electron beam
Gate valve
Skimmer
Quartz nozzle
Transfer line p = 10^{-6} mbar
Sampling loop
Vacuum bypass
He 1.5 bar
GC 1.5 bar
8-way valve
Injection block
Sampling at p = 10^{-1}-10^{-6} mbar

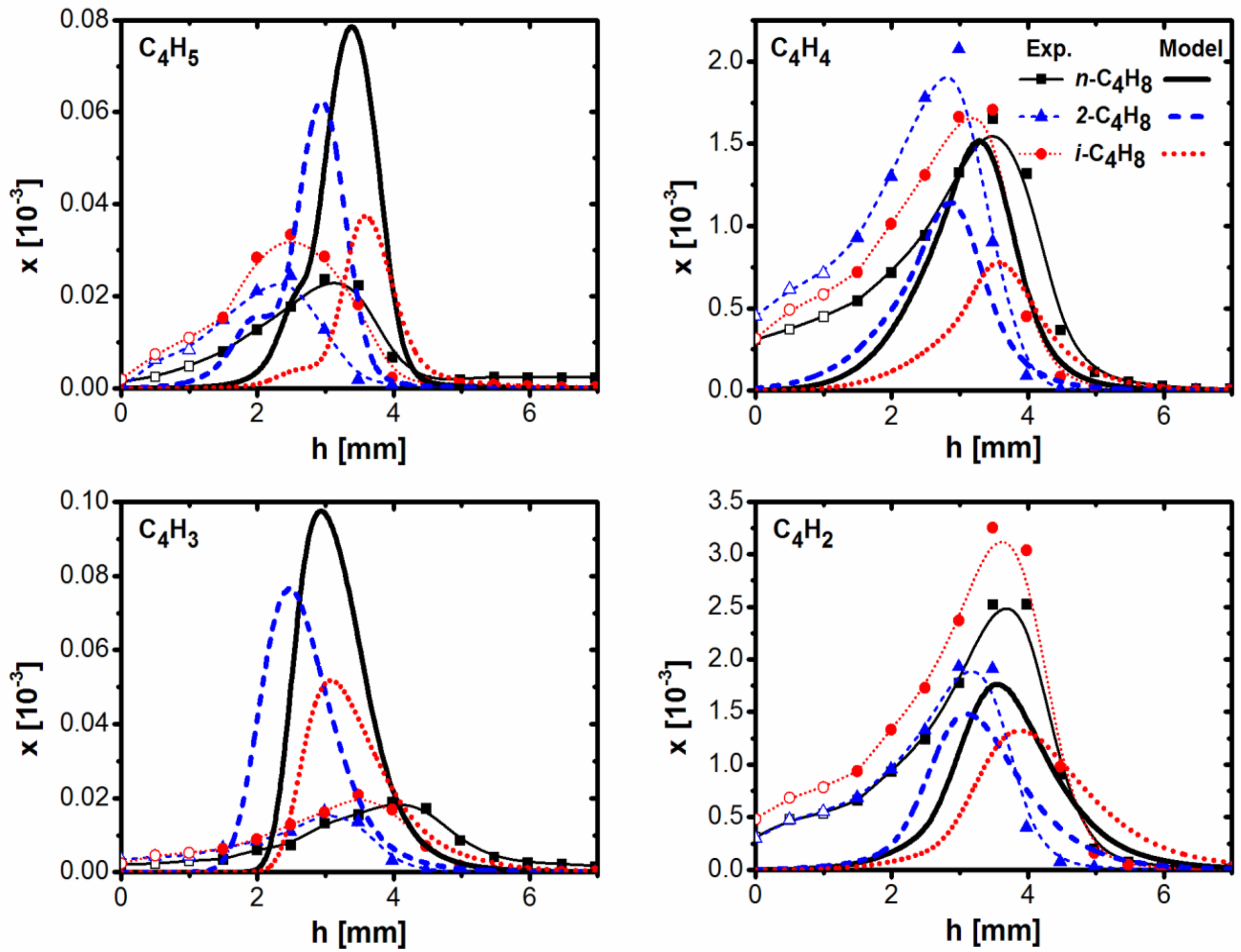
M. Schenk et al, Combust Flame 2012, submitted



- **In-situ isomer separation + EI-MBMS**
- ***Example:* butene flames, C_5H_8 m/z 68**



Butene combustion as C4 chemistry subset



M. Schenk et al, Combust Flame 2012, submitted

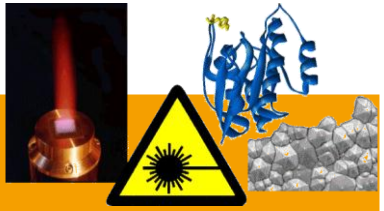
- **Different fuel break-down schemes for the 3 butene isomers.**
- ***C3 route* is of high importance for all butenes, almost exclusive for *i*-butene.**
- **Additional *C4 route* exists for the 2 linear butenes.**

W2P081 Tue

Highly complex chemistry: Biomass pyrolysis

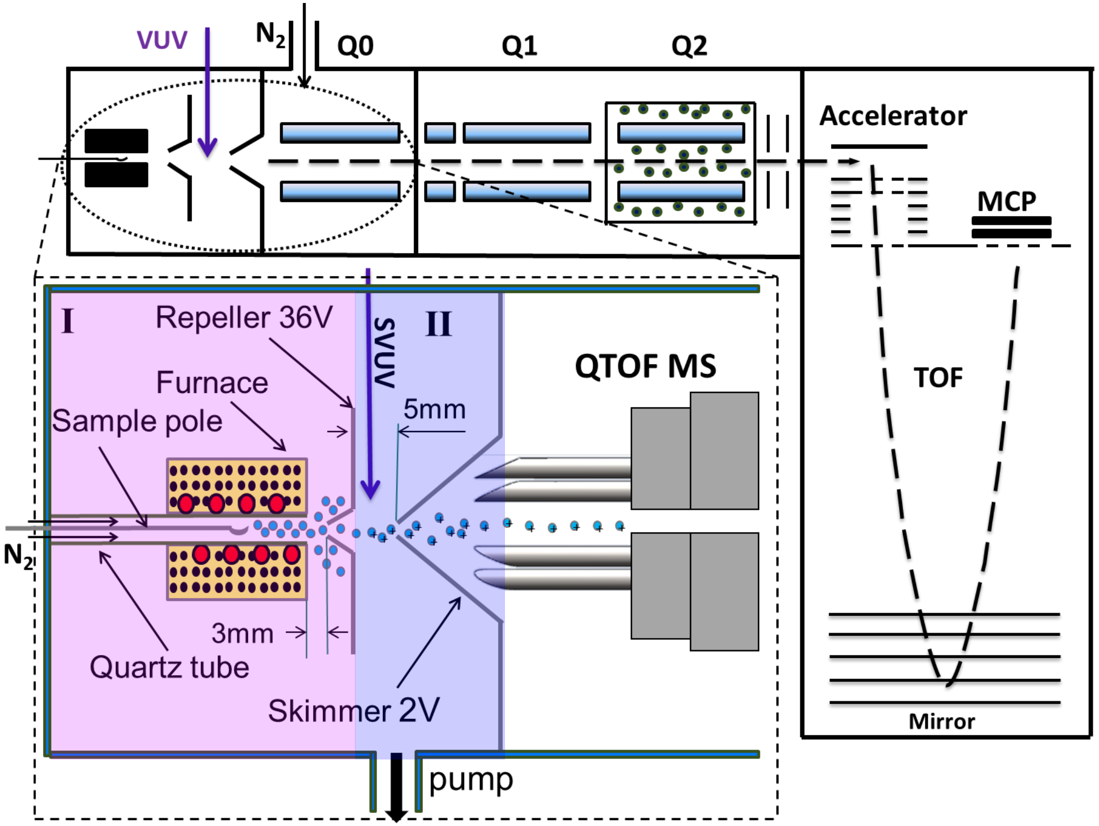
- **Tunable VUV PI-MBMS for analysis of pyrolysis profiles (T, time) of second-generation biofuels.**
- **Fast-growing poplar wood as potential corn replacement; carbon conversion to biofuels.**

J. Weng et al, PROCI 34, 2012



Poplar pyrolysis set-up

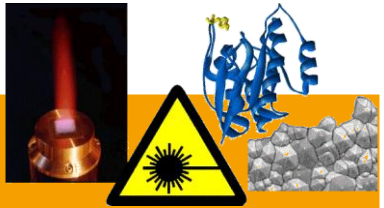
- **Qstar triple quadrupole TOF-MS with mass range 30-20000 Da, *resolution 10000*.**
- **Reactor is heated to specific temperature, then sample inside the quartz pole is pushed into the furnace.**
- **Pyrolysis products pass through a repeller plate into the photoionization region, photoions are analyzed by the QTOF mass spectrometer.**


VUV
N_2
Q0
Q1
Q2
Accelerator
MCP
TOF
Mirror
I
Repeller 36V
VUV
II
QTOF MS
Furnace
Sample pole
5mm
N_2
3mm
Quartz tube
Skimmer 2V
pump

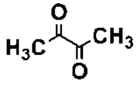
I. Pyrolysis, 20 mTorr

II. Photonization

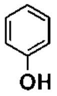
J. Weng et al, PROCI 34, 2012



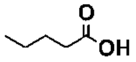
Major products from poplar pyrolysis



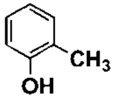
$C_4H_6O_2$ (86) /
2,3-Butanedione



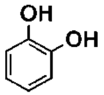
C_6H_6O (94) H
Phenol



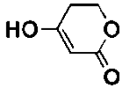
$C_5H_{10}O_2$ (102) /
Valeric acid



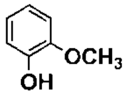
C_7H_8O (108) H
o-Cresol



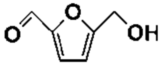
$C_6H_6O_2$ (110) H
Dihydroxybenzenes



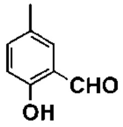
$C_5H_6O_3$ (114) /
4-Hydroxy-5,6-dihydro
-2H-pyran-2-one



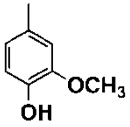
$C_7H_8O_2$ (124) G
2-Methoxyphenol



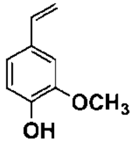
$C_6H_6O_3$ (126) /
5-Hydroxymethyl-
furfural



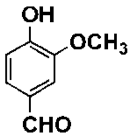
$C_8H_8O_2$ (136) H
2-Hydroxy-5-
methylbenzaldehyde



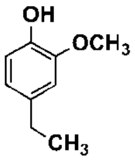
$C_8H_{10}O_2$ (138) G
4-Methylguaiacol



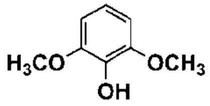
$C_9H_{10}O_2$ (150) G
4-Vinylguaiacol



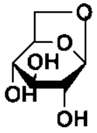
$C_8H_8O_3$ (152) G
Vanillin



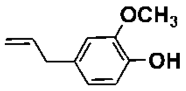
$C_9H_{12}O_2$ (152) G
4-Ethlguaiacol


H₃CO
OCH₃
OH

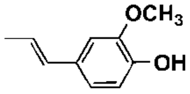
$C_8H_{10}O_3$ (154) S
2,6-Dimethoxyphenol



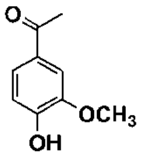
$C_6H_{10}O_5$ (162) /
Levoglucosan



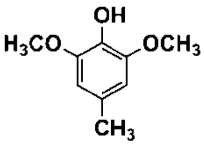
$C_{10}H_{12}O_2$ (164) G
Eugenol



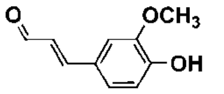
$C_{10}H_{12}O_2$ (164) G
Isoeugenol



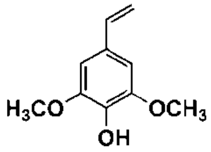
$C_9H_{10}O_3$ (166) G
Apocynin


OH
H₃CO
OCH₃
CH₃

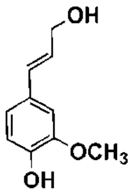
$C_9H_{12}O_3$ (168) S
4-Methyl-2,6-
dimethoxyphenol



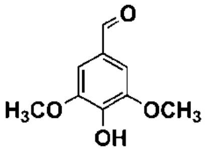
$C_{10}H_{10}O_3$ (178) G
Coniferyl aldehyde


H₃CO
OCH₃
OH

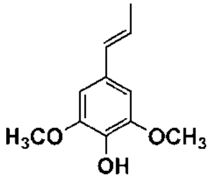
$C_{10}H_{12}O_3$ (180) S
Vinylsyringol



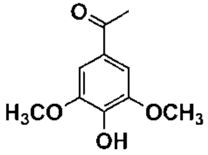
$C_{10}H_{12}O_3$ (180) G
Coniferyl alcohol


O
H₃CO
OCH₃
OH

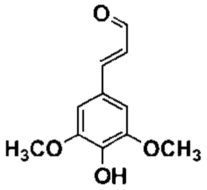
$C_9H_{10}O_4$ (182) S
Syringaldehyde


H₃CO
OCH₃
OH

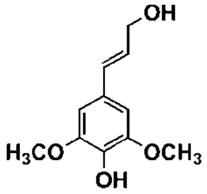
$C_{11}H_{14}O_3$ (194) S
4-Propenylsyringol


O
H₃CO
OCH₃
OH

$C_{10}H_{12}O_4$ (196) S
1-(4-Hydroxy-3,5-dimethoxy
-phenyl)ethanone

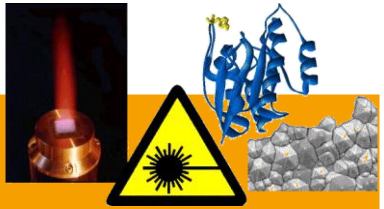

O
H₃CO
OCH₃
OH

$C_{11}H_{12}O_4$ (208) S
Sinapyl aldehyde

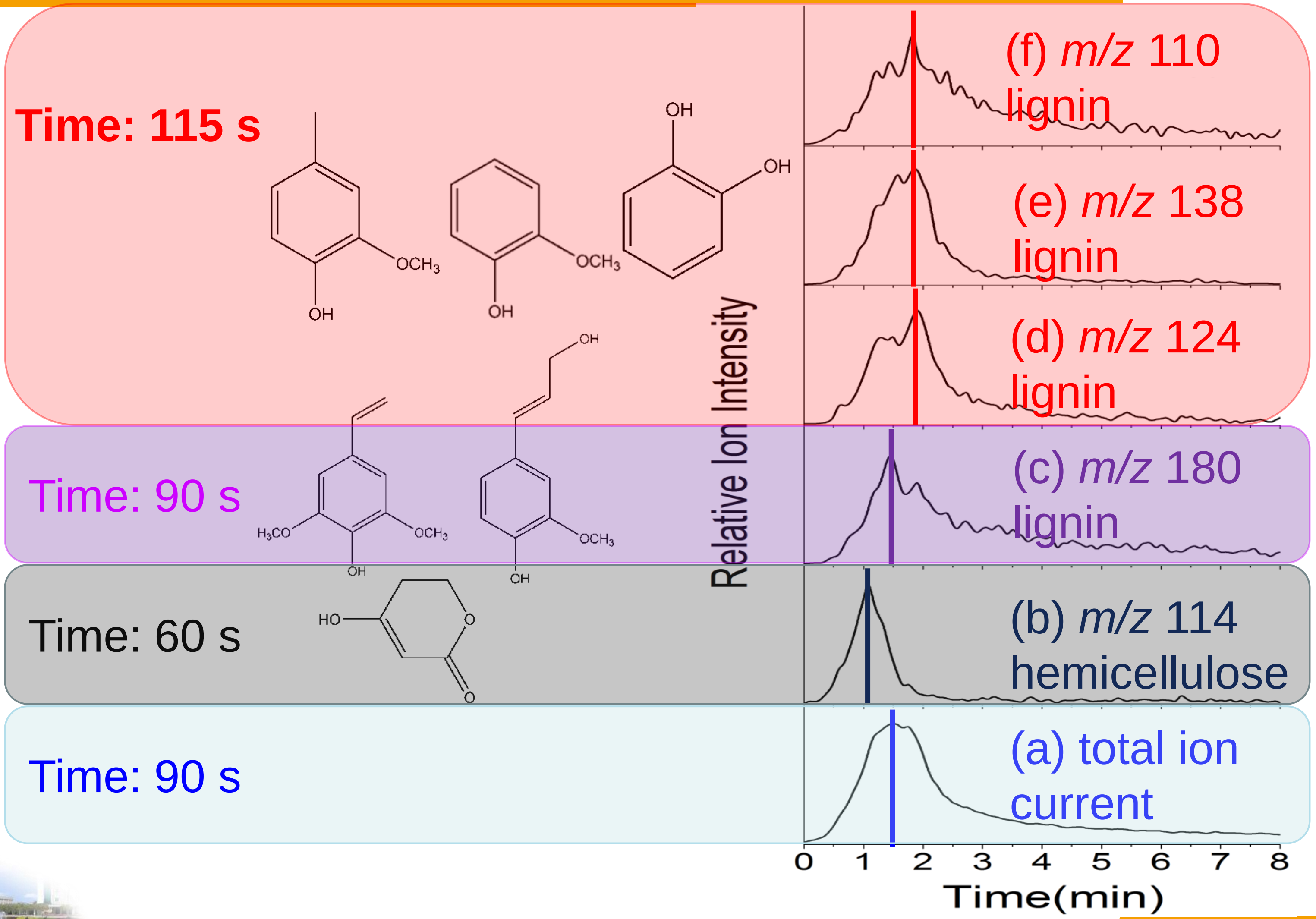

OH
H₃CO
OCH₃
OH

$C_{11}H_{14}O_4$ (210) S
Sinapyl alcohol

J. Weng et al, PROCI 34, 2012



Time-resolved pyrolysis profiles



Time: 115 s

Time: 90 s

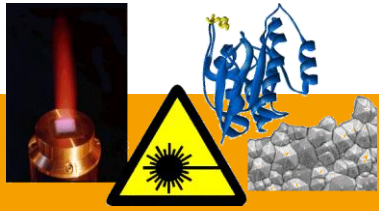
Time: 60 s

Time: 90 s

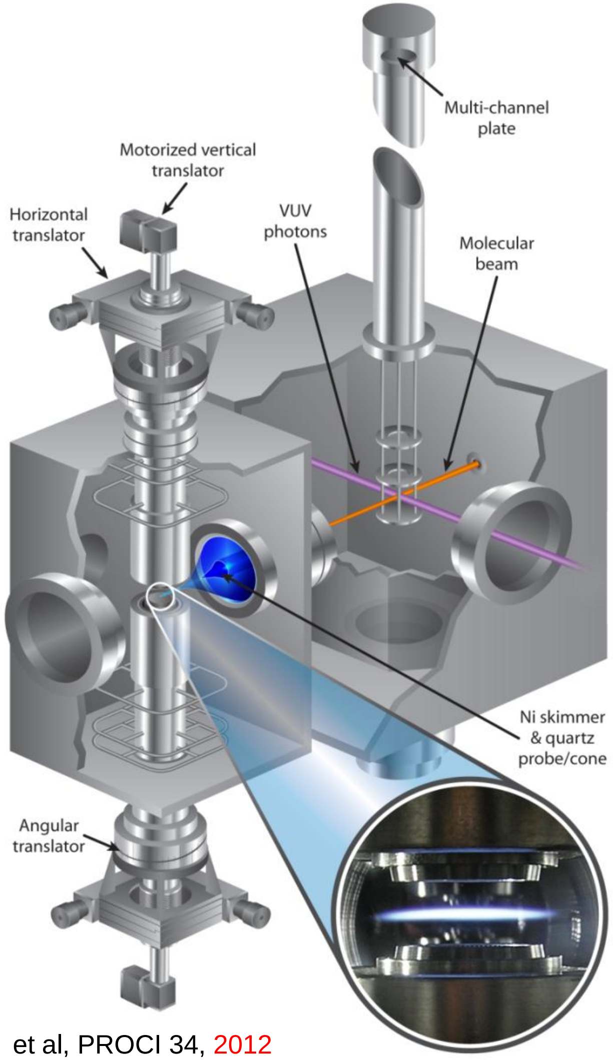
500 °C
10.5 eV

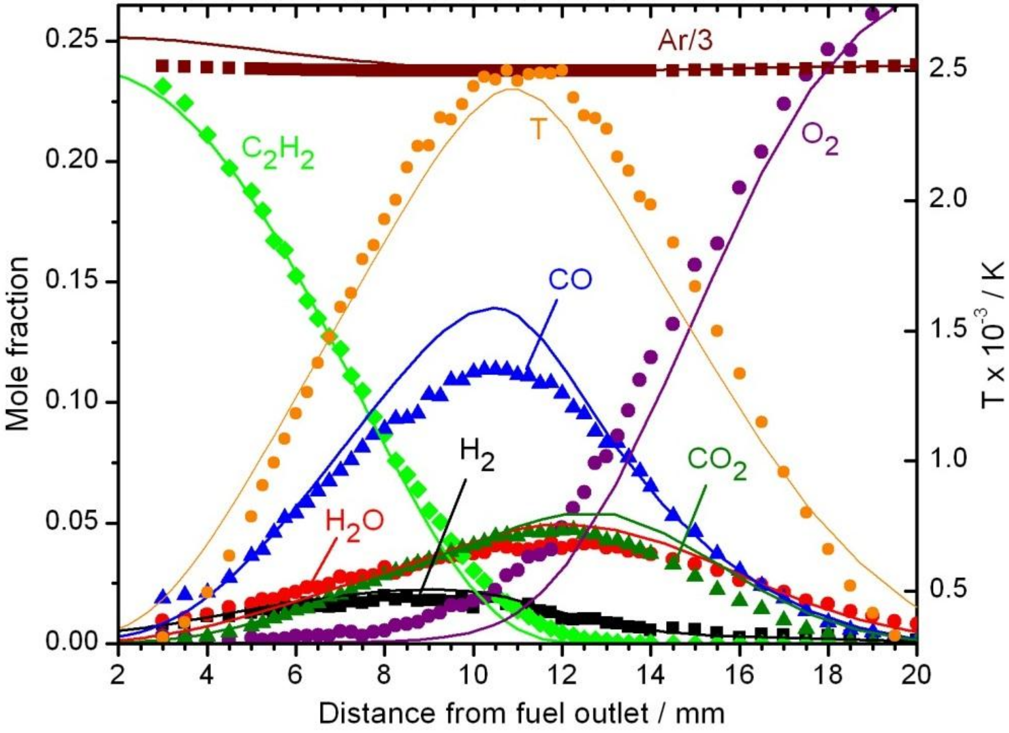
2G10 Tue

J. Weng et al, PROCI 34, 2012



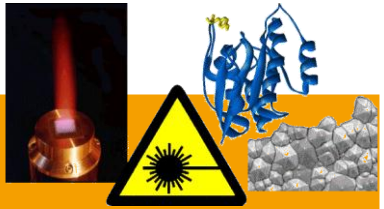
MBMS in non-premixed flames


Multi-channel plate
Motorized vertical translator
Horizontal translator
VUV photons
Molecular beam
Ni skimmer & quartz probe/cone
Angular translator

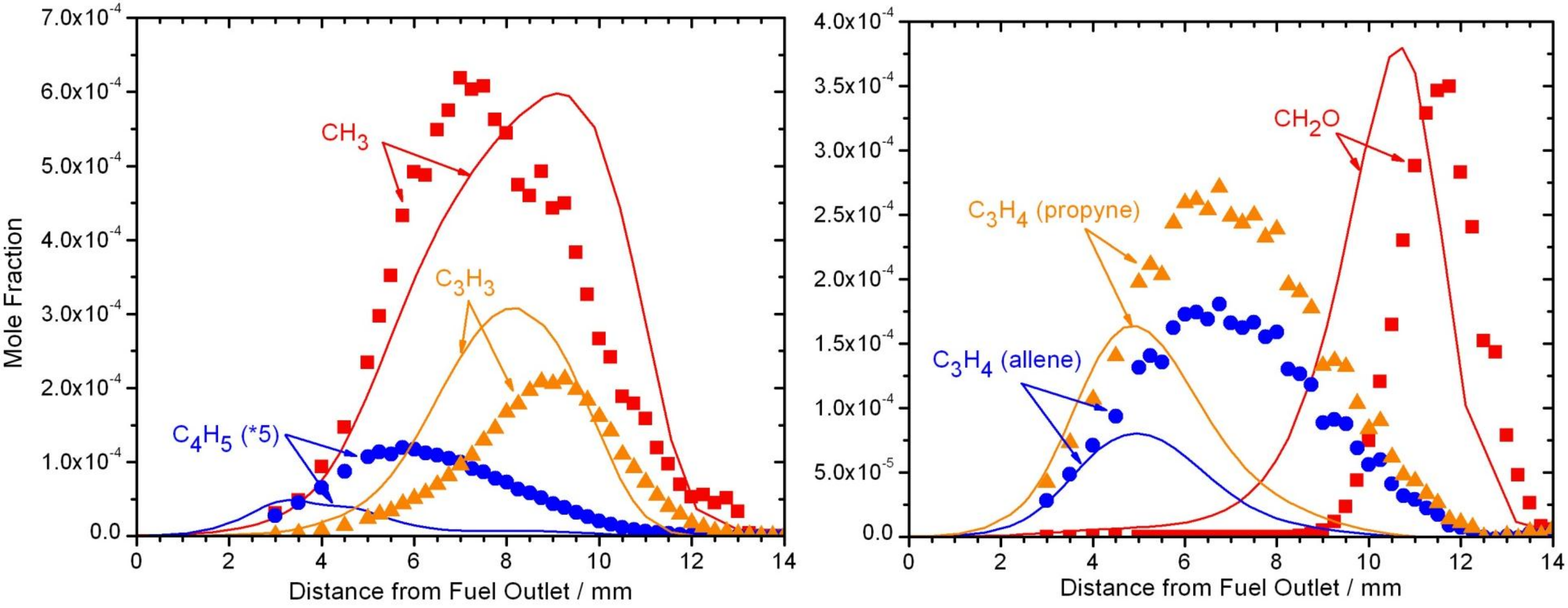


- ➢C_2H_2 flame at 30 Torr
- ➢Mole fractions vs. fuel outlet
- ➢Agreement with model by Jim Miller

S.A.Skeen et al, PROCI 34, 2012



MBMS in non-premixed flames

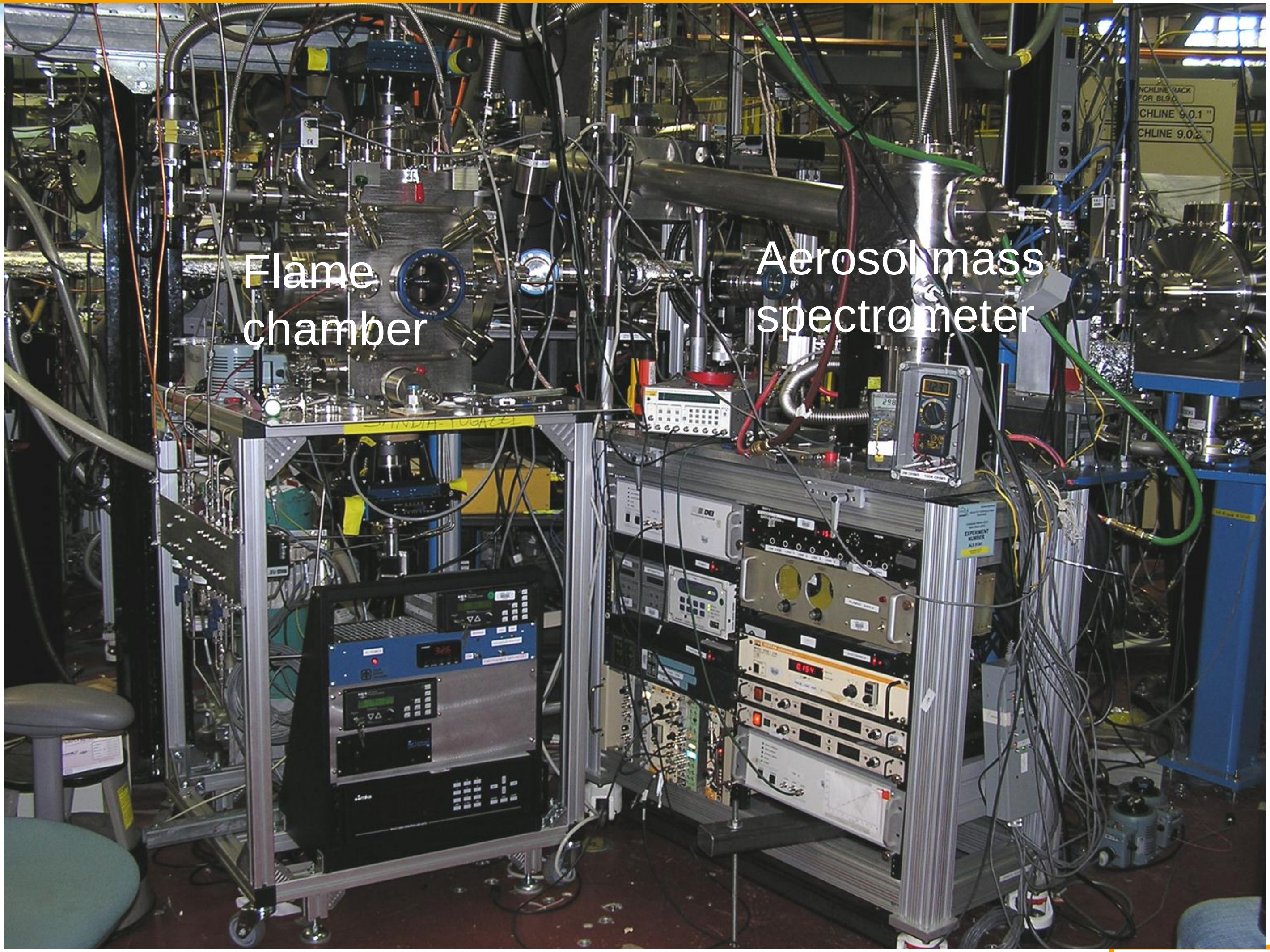


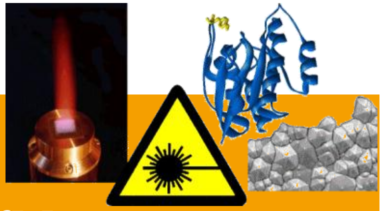
- ➢**Radicals can be detected.**
- ➢**Profiles appear shifted vs. model.**

5E07 Fr

S.A.Skeen et al, PROCI 34, 2012

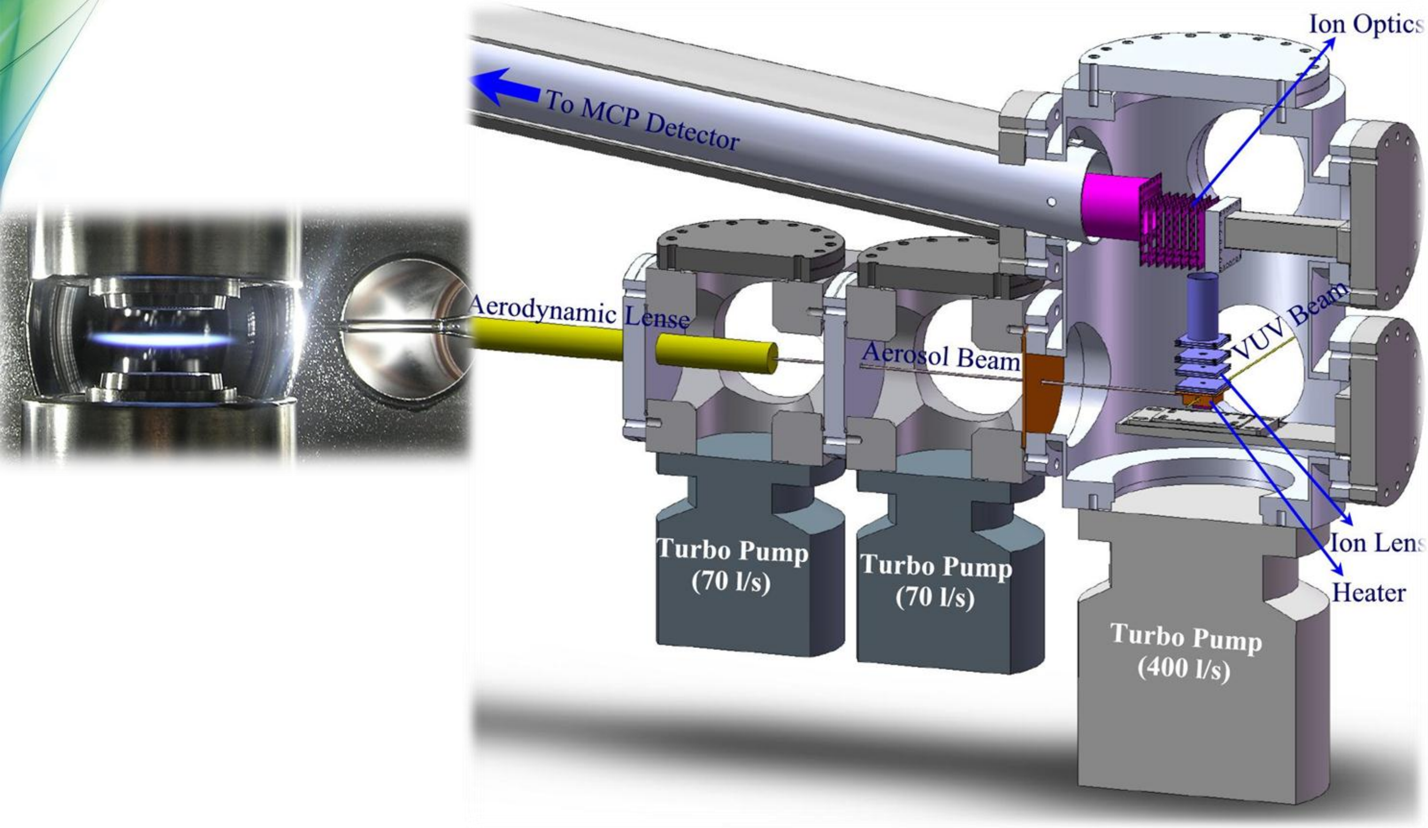
Flame-sampling aerosol mass spectrometry


Flame chamber
Aerosol mass spectrometer

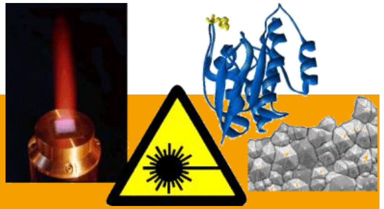


Flame-sampling aerosol mass spectrometry

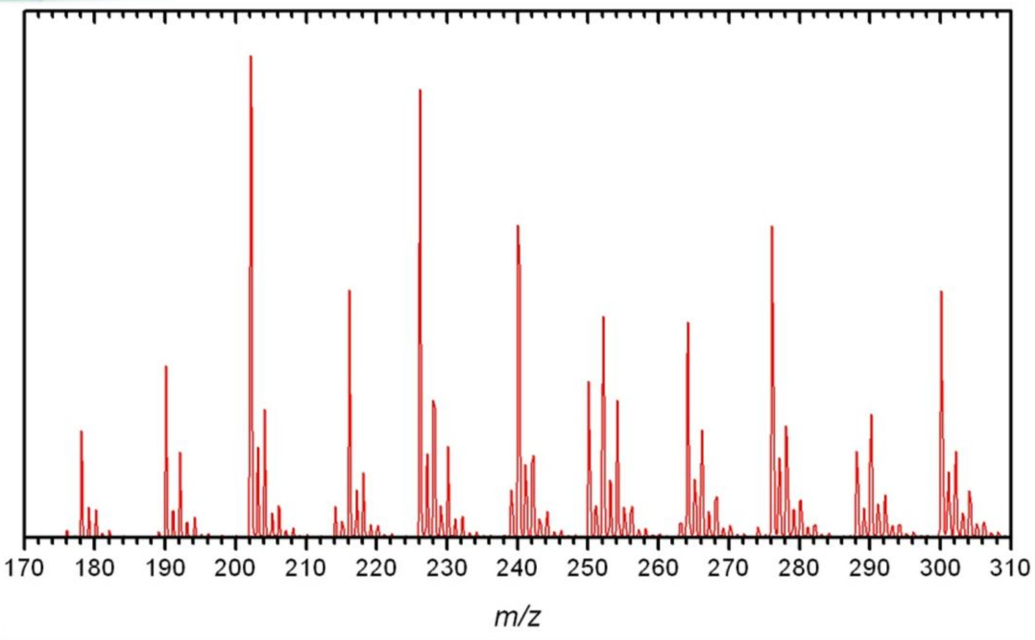
- **Gas phase species and *50-100 nm particles* are sampled from 700 Torr counterflow flame with quartz microprobe.**

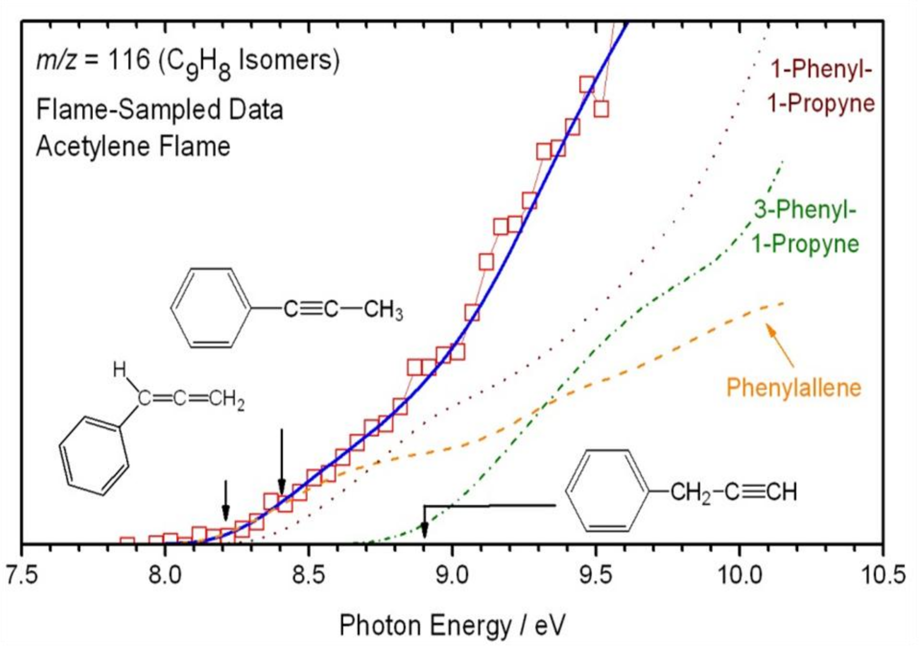

Ion Optics
To MCP Detector
Aerodynamic Lense
Aerosol Beam
VUV Beam
Ion Lens
Heater
Turbo Pump
(70 l/s)
Turbo Pump
(70 l/s)
Turbo Pump
(400 l/s)

- **Particles are focused with aerodynamic lens onto heated copper plate and flash-vaporized.**
- **Molecular constituents are VUV-photoionized and detected by TOF mass spectrometry.**

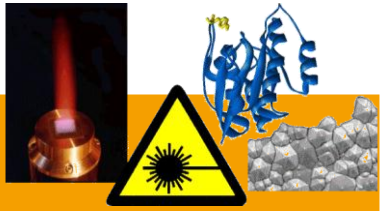


Particle chemical composition: surprises

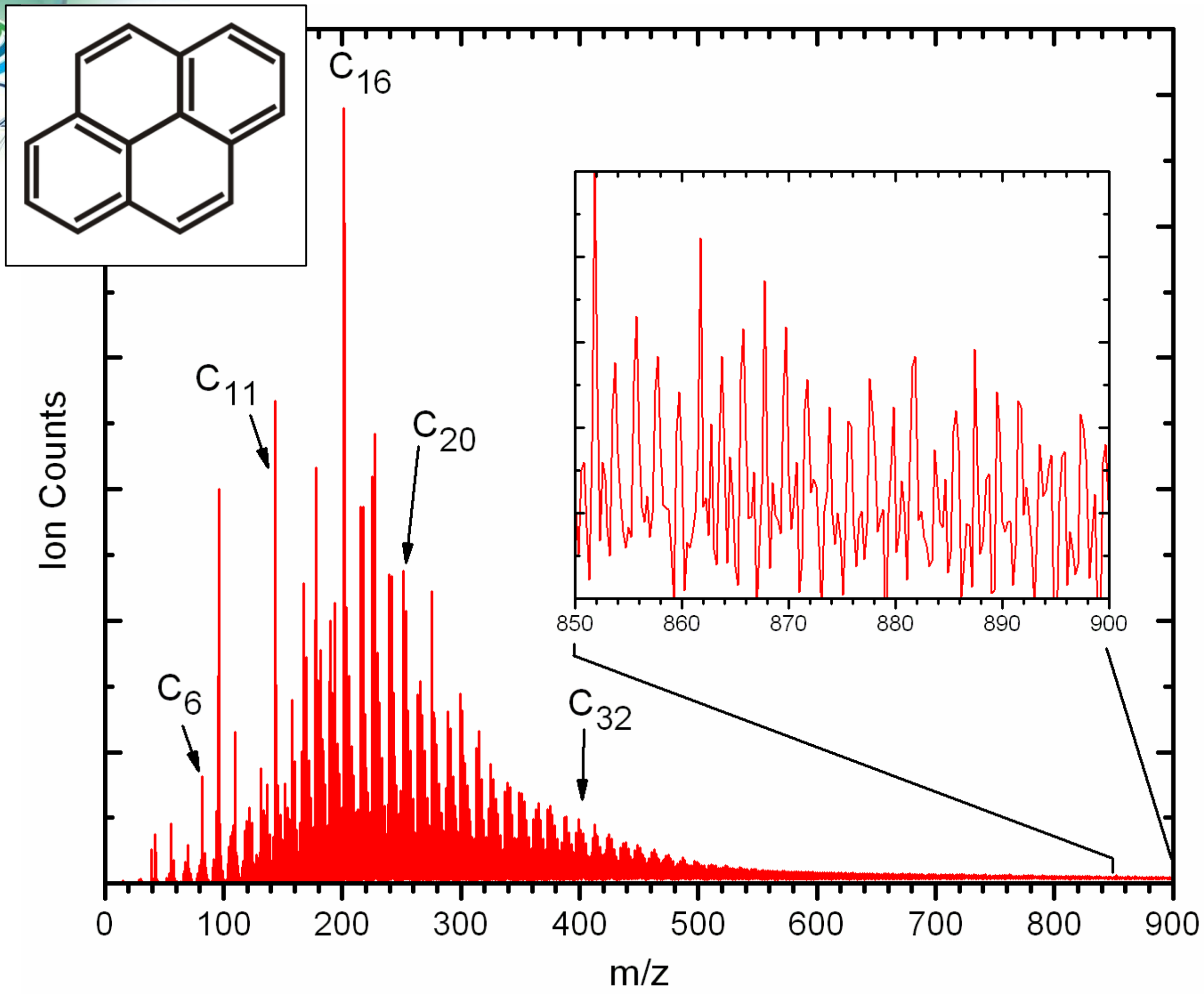




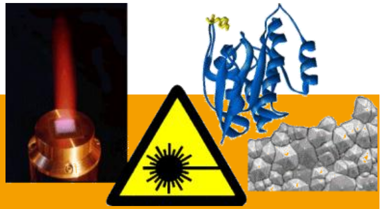
- **Mass spectra map chemical composition of the particles vs. distance from the fuel outlet; PIE spectra permit identification.**
- ***Example*** **m/z=116, normally only identified as indene, but PIE curve shows also *phenyl-substituted allene and propynes*.**



Soot formation beyond benzene

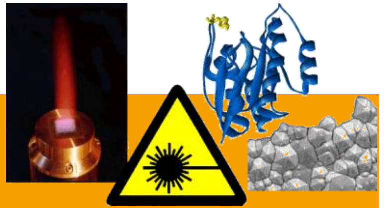


- ➢Many species beyond benzene to ~1000 Da.
- ➢Mass spectra peak at around 202 Da, i.e. pyrene.
- ➢Detailed analysis in progress.



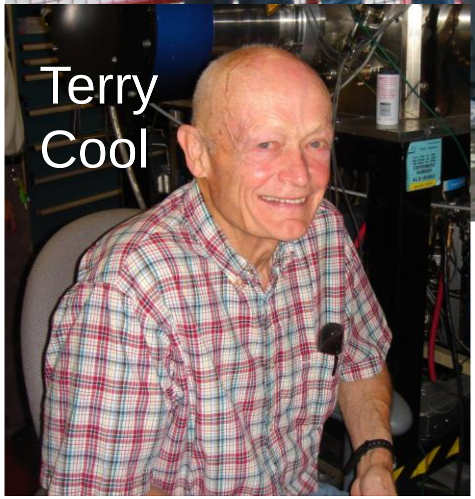
Perspectives: Future trends and needs?

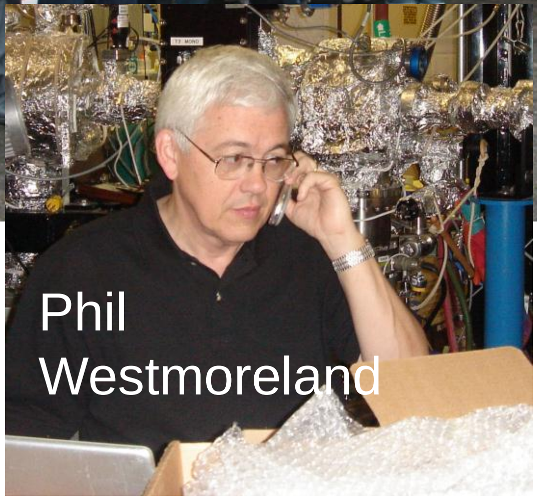
- ***New combustion chemistry:*** **more elements, higher mass range, structure-selective quantitative analysis.**
- ***New measurement domains:*** **larger p and T range, pyrolysis vs. highly-diluted oxidative systems, particles, aerosols, homogeneous vs. heterogeneous combustion chemistry.**
- ***Time-resolved*** **analysis.**
- ***Support by theory:*** **ionization energies, structures, simulation of spectra, kinetics, thermochemistry.**
- ***Combination of methods:*** **optical&MS techniques, in situ GC-MBMS, IR-absorption, MS-MS, PEPICO, ….**
- ***Caveat:*** **Let‘s get sampling problem solved!**



Kai Moshammer
Patrick Oßwald
Friederike Herrmann
Arnas Lucassen
Marina Schenk
Kuiwen Zhang

THANK YOU


Terry Cool


Phil Westmoreland

Nils Hansen
Tina Kasper

Fei Qi

Elementary Kinetics Discussion Summary

Robert Tranter

- A number of topics were discussed extensively. The main points are sumarized on the following slides and some principle points are given below. Interestingly, the group independently arrived at many conclusions similar to those of the Reaction Mechanism discussion group.
- A primary topic of discussion concerned making experimental and theoretical data available in a format that would enable future reevaluation.
- A secondary topic of some concern was the long term status of the NIST kinetics database. All participants in the discussion acknowledged the importance of this database to their research and it is clearly a significant tool for the kinetics research community.
- Concern was expressed, during presentation of the discussion groups findings, that there is only a very limited and shrinking number of people measuring elementary rate coefficients at flame temperatures.

- Sharing Data
  - Common structure for reporting data
    - XML type?
  - Infrastructure
    - PRIME type?
    - More use of supplementary information in journals
      - Attach XML files
      - ASSCII files of data

- NIST Kinetics database
  - What is the current status?
  - What will be the long term availability?
  - Can the Combustion community provide support?
  - Can it made more open to help keep it up to date?
    - Upload your data
    - Feedback forms
    - Wikipedia type approach?

- Areas of need for flame chemistry
  - Low temperature chemistry
  - HO_2 reactions
    - Experiment
    - Theory
  - $R + O_2$
    - Experimental measurements

- Core reaction mechanism
  - C0, C1, C2….
  - Can a definitive set be established?
  - Is a single core mechanism desirable?
  - How would it be maintained and updated?

“Kinetic mechanisms” discussion Summary

Matt Oehlschlaeger

Challenges

- Expense of theoretical and experimental determinations of rate coefficient
  - ~30 rate theoretical rate predictions / year; similar annual experimental yield
  - Not all theoretical predictions are of equal value; QC tools in the wrong hands can be dangerous

- Development and optimization of rate rules for reactions that can't be calculated or measured
  - Is number of rules finite?

Challenges

- Never will be enough data to validate a model across all conditions found in a turbulent flame
  - Need to identify regimes where uncertainty & sensitivity exists
  - Multiple groups perform complimentary experiments
  - (Re)evaluate old data
- At high temperatures
  - Pyroltic chemistry leaves fragments
  - Structure of fuel fragments (olefins) controls their reactivity
  - Design thoughtful experiment to probe these portions of the models; not always necessary to look at parent fuel
- Low temperatures: fuel specific chemistry important
- C_0 chemistry
  - Relatively small uncertainties (~25%) → high cost for small improvements
  - HO_2 chemistry a question, measurements needed

Challenges - What does industry care about?

- Real fuels
  - Blending effects – classes of components
  - Prediction of octane rating for fuel blends
  - Aromatics, olefins
  - N-alkanes (NTC energy release)
  - Alternative fuels farther off than public may think
- Mechanisms
  - Simplicity – number of reactions
  - Rate of heat release, transition from low- to high-T, temperature distribution, NOx, soot, noise (diesel), ignition delay
  - Resolve trends
  - Sensitivity of parameters on operation/performance
- Tools for: model development, surrogate formulation, rate prediction, etc.
  - Methods for dissemination and training
  - Industry is using: not predictive enough for computer design
    - No feedback
    - Little feedback even between kinetics and CFD communities
  - Translation of uncertainties in fundamental properties/predictions to uncertainties in applied outputs (engine performance)

How has the community changed?

- Today’s perception: science will answer everything
- 1979: Irvin Glassman – “this soot problem keeps coming around”
  - Today – soot is still a problem
- First n-heptane mechanism ~1970
  - Still being worked on
  - First N-dodecane mechanism ~1990s
    - Similar fidelity to n-heptane
  - Still work need – NTC/low-T regions

Our work is directed by the problems facing industry

Roadmap/Collaborations

- Common community C_0 model
  - Optimized vs not
  - Dynamic vs fixed vs partially fixed
- Documentation
  - Data must be made available – necessary for simulation of exp
  - Models must be available, documented, and consistent (e.g., forward and reverse rates consistent with thermo)
  - Should further standardization of the requirements for reporting models and experiments exist?
- Cyber infrastructure for data/models/etc.
  - Models and data need to be on web
    - Improve the visibility of our work
    - Historical record of model changes
  - Prime?

Summary of Flame Chemistry Discussion Session at the 1st Flame Chemistry and Transport Workshop

28-29 July 2012
Warsaw, Poland

Chairs:
Timothy Ombrello and Zheng Chen

The Discussions Moved in the Direction of Trying to Understand the Major Roles and Directions with Regard to Flame Chemistry

Validation of Flame Chemistry Through Well Defined Platforms: The Intermediate Users of the Chemistry

What are the Major Burner Platforms?

1. Flat Flame/McKenna Burner
2. Counterflow Burner
3. Spherically Propagating Flame
4. Heat Flux Burner
5. Micro Tube/Reactor Flame
6. "Hencken" Type Burners
7. Others?

Challenges

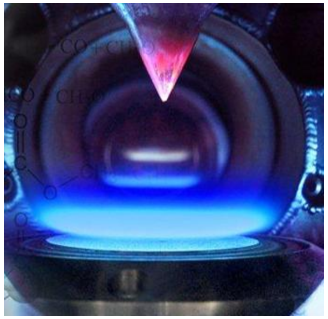
Do these platforms provide the detail and quantification needed?

Can they produce all of the information that is sought?

-Appropriate pressures and temperatures?
-1-D, steady?
-Optical and probe access?

Three Major Types of Platforms Used for Fundamental Flame Studies – Their Strengths and Weaknesses

1. Flat Flame Burner



-$P \approx 0.03$-1 atm
-molecular beam mass spectrometry measurements
-thickened flame zone for better spatial measurements
-how to clearly define B.C.'s, especially when using probes
-losses to burner surface (heat and radicals)
-higher pressures?

2. Counterflow Burner

-$P \approx 0.5$-5 (10?) atm
-ignition, extinction, flame speed measurements
-good optical access
-B.C. problems under certain conditions
-speciation measurements?
-higher pressures?

3. Spherically Propagating Flame

-$P \approx 0.5$-100 atm
-flame speed measurements
-limited to flame speed and structure measurements

Other Relevant Areas of Discussion

Diagnostics

Quantification of new diagnostic techniques

Intrusive vs. non-intrusive measurements, especially at high pressure

- -spatial resolution problems?
- -time scale of measurement and quenching dependence

Transport and Thermo-Chemistry at High Pressure

Challenge of transport parameters of large intermediate species

Can we pull upon rocket community (high P and T)?

Flames provide a means of validation → how can diagnostics help?

Turbulence?

What about turbulence and flame chemistry interaction?

Should this be tackled at this point?

Defining Questions of Discussion

1. Do the current platforms provide data under relevant conditions (high pressure with and without turbulence) with high enough fidelity?

2. Can we think about developing new platforms differently than what was thought of 20-50 years ago because of the advancement of diagnostic techniques?

We Find That There is Not a Lack of Data, But Rather a Lack of Clearly Defined and Quantitative Experimental Data

⇩

How Can We Change?

The Way Forward - Two Paths:

1. Extend current techniques for higher pressure with and without turbulence and careful attention paid to quantification, systematic and measurement uncertainties, application of advanced diagnostics, etc.

2. Develop new “standardized” burner systems for high pressure flame studies
   - -similar to how Sandia developed Turbulent Non-premixed Flames (TNF) library
   - -clearly define boundary conditions
   - -different types of burners to cover range of measurements
   - -start at 1 atm and refine for higher pressures
   - -heating and/or dilution at high pressure to thicken flame for better spatial resolution?
   - -some intermediate between a flow reactor and flame regime?
   - -1-D and steady

The combustion and diagnostics fields have advanced to a point of allowing us to “reinvent” how we think about experiments and their use for development and validation of combustion chemistry.

Poster presentations at the 1st International Flame Chemistry Workshop

1. “One-dimensional (1-D) Nanostructured Metal Oxides for Catalytic Oxidation of Hydrocarbons” by Xiaolin Zheng, Stanford University
2. "A database of small molecule thermochemistry for combustion" by C. Franklin Goldsmith, Gregory R. Magoon, William H. Green, Massachusetts Institute of Technology
3. “Further Developments in Multi-Scale Combustion Models” by M.P. Burke, S.J. Klippenstein, L.B. Harding, C.F. Goldsmith, A.W. Jasper, L. Sheps, O. Welz, J. Zádor, H. Huang, C.A. Taatjes, Argonne National Lab. and Sandia National Lab.
4. “Pressure dependence in the competitive thermal isomerization decomposition of the cyclohexyl radical” by Enoch Dames and Hai Wang, University of Southern California
5. “A Chemical Kinetic Study of the Alternative Transportation Fuel, *tertiary*-Butanol”, J. K. Lefkowitz*, J.S. Heyne, Y. Ju, F.L. Dryer , Princeton University
6. “Direct Numerical Simulations of Multistage Ignition for a Stratified HCCI Engine with Exhaust Gas Recirculation”, by Hossam A. El-Asrag*and Yiguang Ju, Princeton University,
7. “Chemical Kinetic Uncertainty Minimization through Laminar Flame Speed Measurements,” by Okjoo Park, Peter S. Veloo, Hai Wang, Fokion N. Egolfopoulos, University of Southern California
8. A Comparative Kinetic Study of Methyl and Ethyl Ester Oxidation in Diffusion Flames by Pascal Diévart, Jing Gong, Sang Hee Won, Yiguang Ju, Princeton University